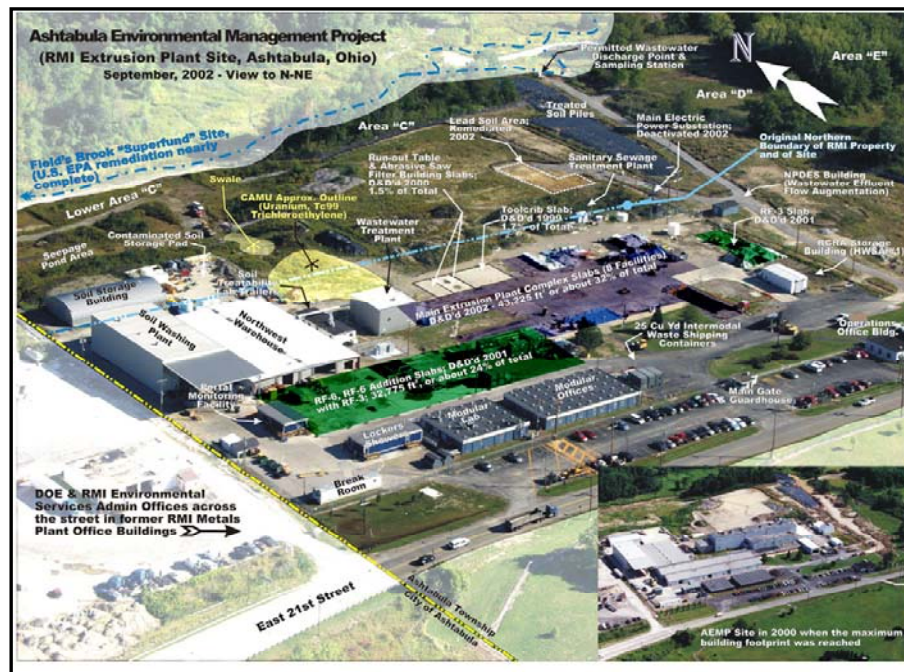# Technical Evaluation of Excavation Based Groundwater Remediation and Alternatives for the Ashtabula Closure Project

Prepared by

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Technical Assistance Team

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Technical Evaluation of Excavation Based Groundwater Remediation and Alternatives for the Ashtabula Closure Project

Ashtabula Ohio, June 24 through June 27, 2003

See Appendix for Technical Team Members and Contributors

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EXECUTIVE SUMMARY

The general objective of the study was to assist the Ashtabula Closure Plant (ACP) in their efforts to develop and refine a comprehensive, technically-sound strategy for remediation of groundwater contaminated with uranium, technetium 99, and trichloroethylene (TCE). To provide the necessary flexibility to the site, the resulting evaluation considered several approaches that assume large scale source excavation and several alternative technologies that assume less extensive source excavation (depending on soil and groundwater cleanup standards).

- The team strongly supports ACP's efforts to develop and implement a comprehensive site cleanup strategy.

- The team endorsed continued development of technically based site specific standards for both soil and groundwater and provided specific input to support the effort from the groundwater remediation perspective.

- The team revisited the current baseline concept – excavation combined with backfill using amendments and a "geodrain" to provide capture of the highest concentration plume. This system was validated as a "viable" option that provides aggressive source removal and provides beneficial plume treatment and containment. Importantly, while the team endorsed the baseline approach as flexible, effective and robust, it is not a complete or comprehensive strategy unless it is combined with MNA documentation and monitoring, or with other technologies such as a distal containment system. Because of uncertainties in amendment performance, a period of active treatment was recommended as a contingency until the data indicated reliable performance.

- Based on geochemical considerations, promising amendment blends were identified. The active ingredients in the top blend were solid phosphate and peat. This blend provides a good combination of geochemical performance and longevity and the amendments are compatible in terms of pH and other factors. Both ingredients are in use and are commercially available. A variety of solid phosphates are potentially usable in this and other amendment blends, but standard hydroxyapatite is probably the most cost effective choice. An alternative amendment for use in an excavation is a liquid organic such as HRC-X or MRC in combination with solid phosphate. This system is more expensive, however, and may require relatively frequent reapplication (every few years). It was not ranked as high as the peat blend. Carefully operated, however, the liquid organic system provides more process control. Other amendment blends were not well matched to the ACP site needs. For example, amendments based on zero valent iron generate high pH water that is not compatible with outfall standards or most other supplementary amendments.

- The team evaluated a several alternatives to the excavation based treatment systems. These alternatives range from aggressive methods such as *in situ* heating down to monitored natural attenuation. Technologies were classified as being "source treatment", "plume treatment" and/or "plume containment". Many of the technologies were found to be viable for the ACP site.

- The most promising of the viable source treatment technologies was *in situ* bioremediation using lactate or HRC. Importantly, the team felt that the data from the existing period of injection are inconclusive. Any decision for further use should be based on additional targeted data collection and ACP should consider restarting injections only if the past results demonstrate that the bioremediation performance will be sufficient to meet site goals and timeframes. Because of the potential for uranium reoxidation, the site should consider addition of phosphate (either inorganic phosphate solution or alkyl phosphate ester). This would enhance long term uranium stability. If bioremediation is shown to be effective based on unambiguous data, its implementation would result in potentially significant cost savings versus most of the alternative source removal concepts.

- The team felt that the most promising plume containment or treatment option was a downgradient interceptor trench optimized for the unique flow system at ACP. The trench would be installed near the edge of the escarpment down through the oxidized till that appears to be the primary transport pathway. As a containment, this trench is likely to be quite effective and could be used or in combination with other technologies (source treatment, plume treatment…) as needed to meet ACP goals for treatment duration and cost. The system could be outfitted similarly to a central excavation and geodrain and fitted with treatment amendments. The same optimal amendments were recommended by the team.

- In all of the categories, the team identified several alternative viable options with some detail on the relative strengths and weaknesses.

- Several supplemental beneficial activities were identified by the team such as engineering the drainage of the site to minimize infiltration and mitigating water line leaks and other sources of anthropogenic water.

- The options and supplemental activities recommended should provide flexibility and assist ACP as they generate a groundwater strategy that optimizes environmental protection, facilitates rapid implementation and contains costs.

INTRODUCTION

General Information

This report presents the results of a technical assistance study to technically evaluate excavation-based groundwater remediation and alternatives at the Department of Energy's (DOE's) Ashtabula Closure Project (ACP). The technical assistance team met in Ashtabula, Ohio from June 24 through June 27, 2003. The effort was sponsored by the DOE Office of Science and Technology (EM-50) Closure Site Technical Assistance Program and was conducted at the request of the Department's Ohio Field Office. The technical assistance team that included experienced professionals in the fields of geology, hydrology, geochemistry, groundwater remediation, and soils technology. Assisting with the study were personnel of the site remediation contractor, RMI Environmental Services (RMIES) along with the ACP RCRA Corrective Action Project Manager from the Ohio Environmental Protection Agency (EPA).

Objective

The purpose of the study was to assist ACP in their efforts to develop and refine a comprehensive, technically-sound strategy for remediation of groundwater contaminated with uranium, technetium 99, and trichloroethylene (TCE). The team initially focused on the current baseline approach – excavating the highest concentration source material followed by implementing hydraulic control and treatment using the access provided by the excavation. The strategy is termed "excavation based" treatment in this report since the beneficial reuse of the excavation as part of the subsequent plume control is a central feature. The initial technical assistance request and scope is presented in Appendix B. Recent progress related to development of technically based site specific soil cleanup standards, if accepted by regulators and stakeholders, suggest that the amount of potential source excavation necessary to protect human health and the environment may be less than the current baseline*. As a result, the scope of the effort was expanded to include alternatives to the excavation based treatment strategies.

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* A value analysis study sponsored by the Closure Site Technical Assistance Program of DOE-EM was held at the ACP from June 17 to June 20, 2003 and focused on validating the results of the RESRAD (residual radioactivity) computer code modeling of the ACP recently performed by SAIC. The study examined the basis for the current ACP 30 pCi/g cleanup standard for total uranium in soil, and found that the clean-up level for total uranium limit could potentially be raised to 125 pCi/g while protecting groundwater to meet the concentration limits. Based on the results ACP requested examination of remedial strategies that might be acceptable if this change in the uranium cleanup level is accepted

Background

In 2002, DOE and RMIES sponsored a general technical assessment of ACP, including the waste management unit (WMU) source and associated groundwater plume that is the subject of this report. Since that time, the results have been used by RMIES as a resource for their environmental management efforts at the facility. Two major recommendations of the evaluation were: 1) consider developing technically based site specific soil and groundwater cleanup standards to support decision making, and 2) consider opportunities for comprehensively linking activities to support environmental management.

The first recommendation supports targeting resources and efforts to those activities that transition the site to an agreed end-state that is protective of human health and the environment. A specific example of the second recommendation was for ACP to consider utilizing infrastructure and access resulting from any necessary excavation as a resource to improve remediation of the residual groundwater plume. It was recognized that efforts toward these two goals are interrelated and that optimization and linkage of field activities are influenced by the any changes due to development of technically based goals and standards. While this interrelationship introduces some complexity in progressing toward final selection and implementation of remediation options, ACP has actively pursued both recommendations. Notably, ACP is developing a range of cleanup options that can be implemented conditionally, depending on the results of the standards and goal setting efforts. A technical assistance team was assembled to assist in this process and to suggest specific technologies and combinations of technologies for different end state objectives. The team had an overall responsibility to refine the earlier recommendations related to cleanup technologies for groundwater and provide more detail. To provide the necessary flexibility to the site, the resulting evaluation considered approaches that assume large scale source excavation and those that assume less extensive source excavation (depending on soil cleanup standards).

CRITICAL OR UNRESOLVED ISSUES

Critical or unresolved issues are site-specific concerns that may impact on remedial performance or decision making. The team identified several broad issues.

- The team strongly supports continued development of technically based site specific standards for both soil and groundwater. The recent RESRAD effort is a reasonable step in this direction. Specific issues that will need to be addressed to support further progress in this area include: modify modeling approaches to adequately represent the potentially significant flow in heterogeneities within a low permeability matrix, factor in other impacts of low permeability in the contaminated zone, work with regulators and stakeholders to develop an appropriate and mutually agreed end state (e.g., brownfield versus free release), and the like. Care should be taken to assure that soil standards and groundwater standards are consistent with each other.

- The team strongly supports ACP's efforts to develop a comprehensive site cleanup strategy. Specific issues that will need to be addressed to support this effort include definition of acceptable points of compliance, remediation time frames, life cycle costs and cost profiles. The team recommends that the strategy include the entire sequence of activities – including source treatment (as needed), plume treatment and containment (as needed), and monitored natural attenuation. The general principles for transition from one stage to the next should be developed based on ACP site constraints and these principles then used as the bases for selecting the final technology mix in the strategy. Various individual technologies and key selection criteria are described in the evaluation section of this report to assist in the effort.

- There is a need to develop a clear conceptual model of contaminant distribution and migration mechanisms, as well as plume structure to improve understanding of the source zone, fate and transport of contaminants, and provide opportunities for focused and optimized remediation. For example, there is a specific need to consider flow in the sand and silt lenses of the upper oxidized till rather than flow through the low permeability section. This non-standard exposure pathway may dominate potential exposure but may also provide some of the best opportunity for cost effective plume treatment.

EVALUATION

Geochemical Evaluation of Potential Amendments for Use **In Situ** *or in* **Capture Systems**

The choice of amendments for a groundwater treatment system must accommodate a number of factors. The amendments must effectively degrade or stabilize the contaminant or contaminants. Their effectiveness must last long enough to outlive the problem or at least long enough so that maintenance costs are minimal. The longevity is affected by reactions with the contaminant, but more importantly by reactions with major ions in solution. Thus, the bulk chemical composition of the contaminant plume is important. If installed in a permeable reactive barrier from which water flows through the amendments and then enters the native soil, the amendments must be compatible with local mineralogy. Likewise, if groundwater flowing through the treatment system discharges to a seepline, stream or outfall, the amendments must be compatible with regulatory limits on these waters. Choosing amendments that meet all of these criteria is difficult, but of paramount importance to success of a treatment system.

Combining amendments in a treatment system compounds the difficulty, but may be necessary to achieve clean-up goals for multiple contaminants. An amendment that is highly effective for one contaminant may render a second amendment ineffective for its target contaminant. This may happen because the first amendment causes coating of the second amendment or changes the chemistry of the second target contaminant. An amendment may also cause concentrations of constituents from the second amendment to exceed regulatory limits. These additional factors must be considered if amendment combinations are used.

Trichloroethylene (TCE) Chemistry

Trichloroethylene (C_2HCl_3) is a chlorinated solvent commonly used as a degreasing agent or cleaner in industrial processes. It acts predominantly as a nonpolar compound, but its slight polar character does allow a solubility of 1100 mg/L in water. As with other nonpolar compounds, the primary adsorbent for dissolved TCE in groundwater systems is natural organic matter. Dissolved TCE can be degraded, and thus remediated, by reductive dechlorination or oxidation. These processes can be accomplished either biotically or abiotically. Biodegradation of TCE is discussed in detail in a later section. Abiotic degradation of TCE is achieved with strong reagents such as zero-valent iron (reductive dechlorination), hydrogen peroxide (oxidation), or permanganate solutions (oxidation).

Uranium Chemistry

Uranium chemistry is complicated by formation of multiple oxidation states and aqueous complexes (Figure 1). In solution, uranium can exist as U(IV), U(V) or U(VI). At low to intermediate pH, U(VI) exists as the uranyl ion, $UO2^{+2}$. At pH of about 8, U(VI) speciation becomes dominated by carbonate complexes that are either neutral or negatively charged and are relatively mobile in the subsurface. There is a large field of dominance for U(V) as UO_2^+, though this species readily converts to either U(IV) or U(VI). U(IV) forms hydroxyl complexes that range in charge from +2 to –1 between pH of 2 and 8. Formation of neutral and negatively charged complexes at pH above 8 enhances the mobility and solubility of uranium. The heavy dashed line represents the boundary

between dominance of carbonate and dominance of methane. Thus, carbonate is reduced below this line and U(IV) hydroxyl complexes are the dominant uranium species.

The two general methods for stabilizing uranium in the subsurface are sorption and manipulation of uranium phase solubility. In natural systems uranium binds strongly to organic materials that range from petroleum bitumen (Curiale et al., 1983) to lignite (Vassiliou, 1980; Ilger et al., 1987). Nakashima et al. (1984) found that the association of uranium to natural organic matter involved both general mechanisms. In their studies uranium was initially sequestered in lignite by formation of urano-organic compounds followed by reduction of U(VI) to less soluble U(IV). The association of uranium with organic matter has become the basis for using organic materials for removing dissolved uranium from water (Heitkamp and Wagener, 1982; Cullen and Siviour, 1982; Morrison and Spangler, 1992). Reduction of uranium to low solubility U(IV) phases by inorganic media has also been effective. O'Loughlin et al. (2003) demonstrated uranium reduction by green rusts, a mixture of ferrous and ferric hydroxides. Likewise, zero-valent iron has been used to reduce uranium (Cantrell et al., 1995; Morrison et al., 2001; Morrison et al., 2002). Another method of promoting uranium precipitation is by addition of ligands that form low solubility phases with U(VI) or U(IV). The most common of these is phosphate (Gauglitz et al., 1992; Jeanjean et al., 1995; Thomas and Mackaskie, 1996; Roig et al., 1997).

Uranium concentrations in ACP groundwater are relatively low and this may limit the options for uranium stabilization. Though concentrations range up to 12,400 ug/L in the WMU area, most are below 2000 ug/L. Figures 2 and 3 show calculated saturation indices for several uranium oxide, hydroxide, and phosphate phases under oxidizing and reducing conditions. These were calculated using the United States Geological Survey code PHREEQC version 2.6 (Parkhurst and Appelo, 1999). For all calculations, a dissolved uranium concentration of 2000 ug/L was used and the water was equilibrated with hydroxyapatite and 0.01 moles of CO_2 at a partial pressure of 0.01 atm. To maintain oxidizing conditions the water was equilibrated with 0.2 atm. of oxygen. Reducing conditions were maintained by equilibrating with elemental carbon. Under oxidizing conditions, the only phase that exceeds saturation is $(UO2)_3(PO_4)_2:4H_2O$ within a narrow pH range of 5.5 to 7.25. Under reducing conditions, uraninite exceeds saturation throughout the pH range from 4 to 12. The phosphate phases, ningyoite and $U(HPO_4)_2:4H_2O$, are saturated at pH less than 8. This suggests that a successful strategy for stabilization of uranium would be reduction in the presence of hydroxyapatite at pH less than 8.

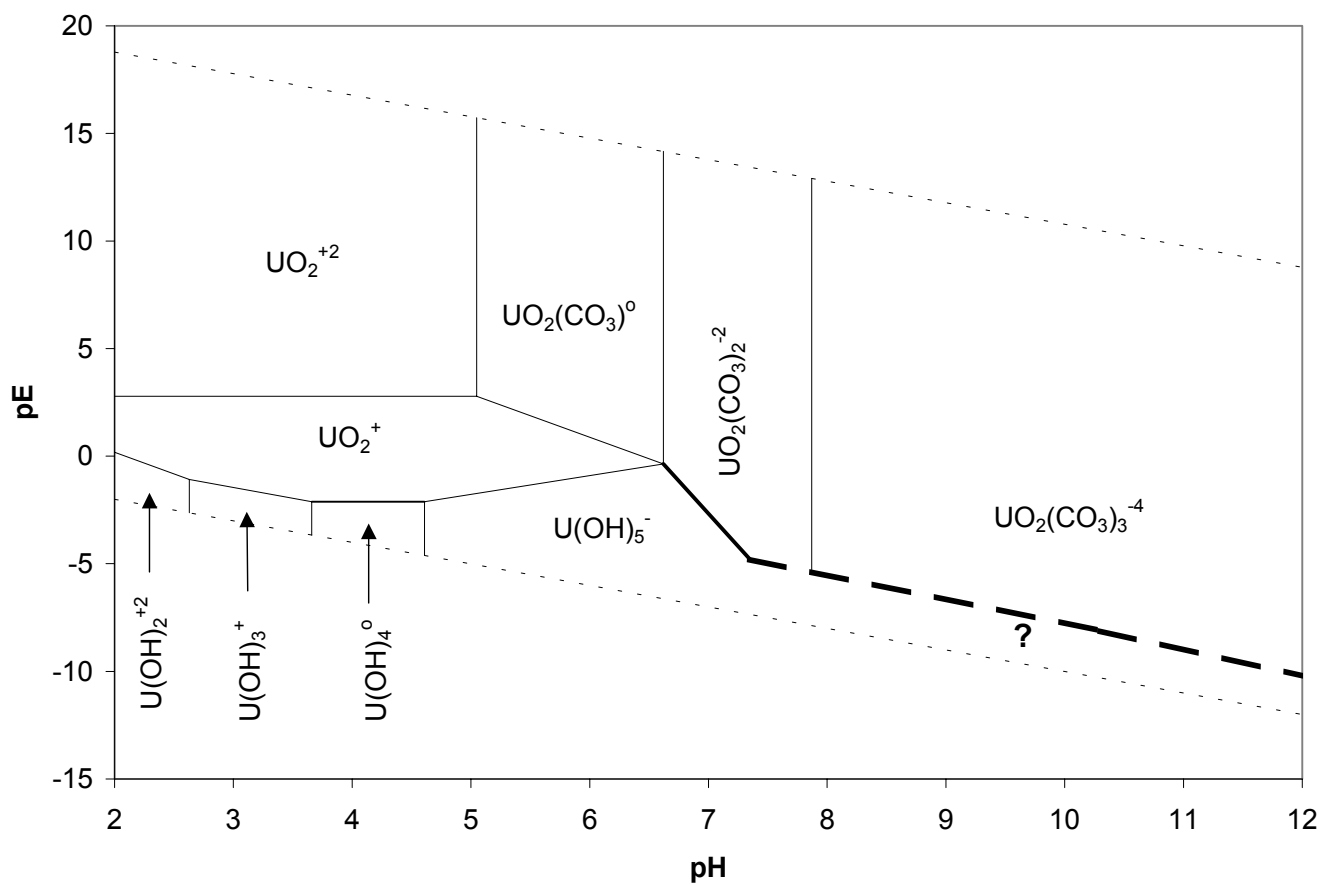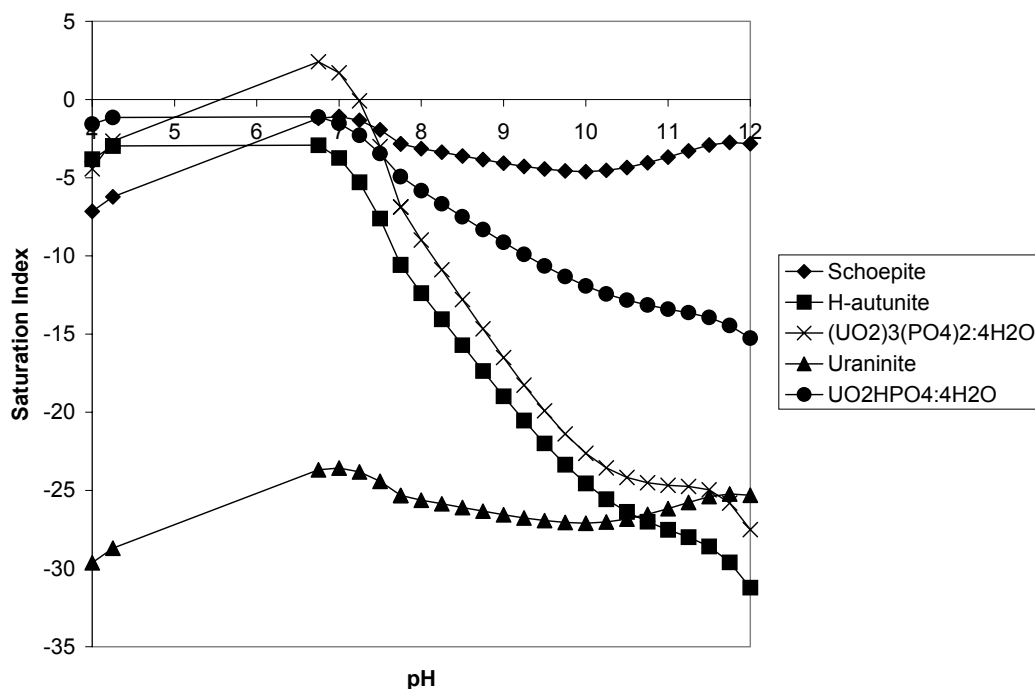**Figure 1. Speciation of uranium at PCO$_2$ = 0.01 atm.**

Figure 2. Saturation indices versus pH for several uranium phases under oxidizing conditions.
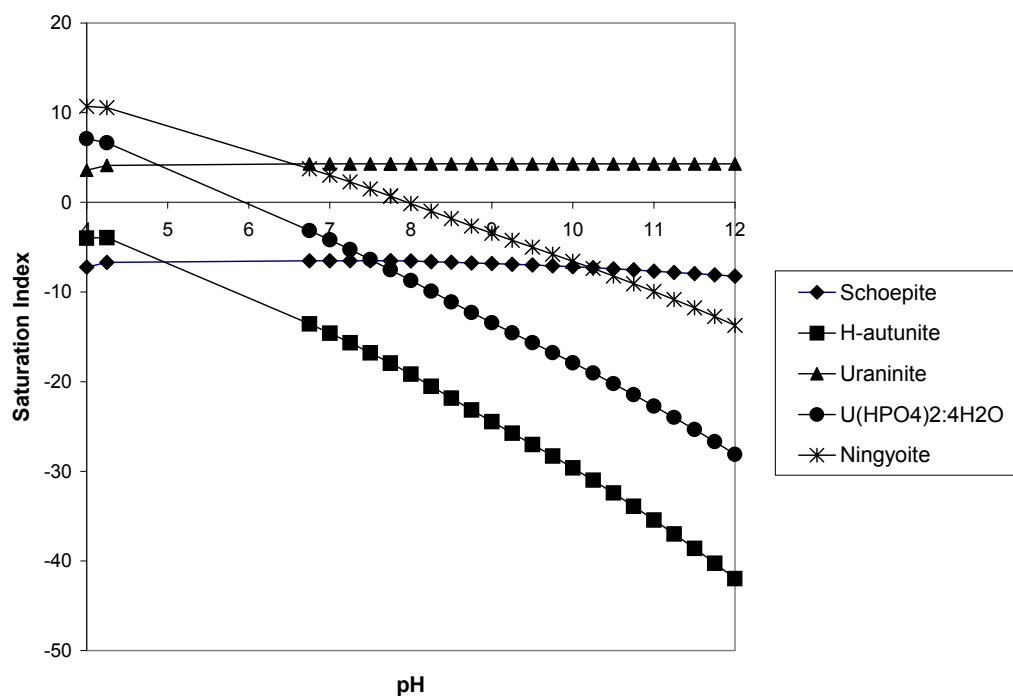

Figure 3. Saturation indices versus pH for several uranium phases under reducing conditions.

Technetium Chemistry

Technetium can exist in multiple oxidation states that range from –1 to +7. The most prevalent forms in groundwater are Tc(IV) and Tc(VII). The Tc(VII) form is generally soluble and dominated by the species TcO_4^- throughout the pH range of 2 to 10. Tc(IV) is much less soluble and tends to form the oxide TcO_2 or a hydrated phase $TcO_2 \cdot nH_2O$. Figure 4 shows the speciation of technetium as a pE versus pH diagram. At mildly reducing conditions, TcO_4^- is reduced to Tc(IV) that hydrolyzes to form $TcO(OH)^+$ and $TcO(OH)_2^o$. At low pH technetium speciation is dominated by TcO_4^-, whereas $TcO(OH)_2^o$ dominates at high pH. This complicates ^{99}Tc remediation because various portions of a plume may be dominated by different species that respond differently to particular remediation methods. In the intermediate pH range both species may exist, further complicating remediation.

One approach to remediation of ^{99}Tc is to reduce it to the Tc(IV) state to precipitate the relatively insoluble oxides. The reduction can be done chemically or by stimulating microbes that reduce technetium. Chemical reduction by aqueous solutions of sodium dithionite has been studied extensively at the Hanford site (e.g. Amonette et al., 1994; Williams et al., 2000). Other aqueous solutions such as those containing Fe(II), Cu(I), or Sn(II) may also reduce technetium, though Cui and Eriksen (1996) found that reduction by Fe(II) was quite slow. The Natural and Accelerated Bioremediation (NABIR) program of DOE has funded several projects to microbially reduce technetium. Examples can be found on the NABIR website http://www.lbl.gov/NABIR.

Any decrease in ^{99}Tc concentrations caused by reduction of Tc(VII) to Tc(IV) is likely to be due to enhanced sorption rather than precipitation of a stable phase. In Figure 5 the solubilities of TcO_2 and $TcO_2 \cdot 1.6H_2O$ are shown versus pH. Though the solubility of TcO_2 is much lower than the solubility of $TcO_2 \cdot 1.6H_2O$, TcO_2 does not precipitate readily at low temperatures. For example, Meyer and Arnold (1991) found that $TcO_2 \cdot 1.6H_2O$ was the stable stoichiometry of the solid phase precipitated by electrodeposition. This is consistent with other studies. Nevertheless, ^{99}Tc concentrations may decrease upon reduction to Tc(IV) because of enhanced sorption of the aqueous species $TcO(OH)^+$ and $TcO(OH)_2^o$ (Walton et al., 1986; Lieser and Bauscher, 1987; Liang et al., 1996). Another reduction option is to reduce Tc(VII) to sparingly soluble Tc metal.

The two solid amendments that have proved to be effective for removal of ^{99}Tc from groundwater are activated carbon and zero-valent iron. Gu et al. (1996) found that activated carbon was an effective adsorbent for TcO_4^- over a wide range of pH. The range of Kd values for the activated carbon exceeded 10^4 ml/g. Zero-valent iron is the primary reductive solid amendment that has been considered for ^{99}Tc remediation. Liang et al. (1996) demonstrated rapid removal of ^{99}Tc from groundwater by reduction to Tc(IV) in the presence of zero-valent iron. They concluded that the decrease in ^{99}Tc concentrations was the result of sorption of Tc(IV) aqueous species rather than precipitation or co-precipitation. Korte et al (1997) also reported effective removal of ^{99}Tc from groundwater by zero-valent iron, but concluded that reductive precipitation was the primary removal mechanism.
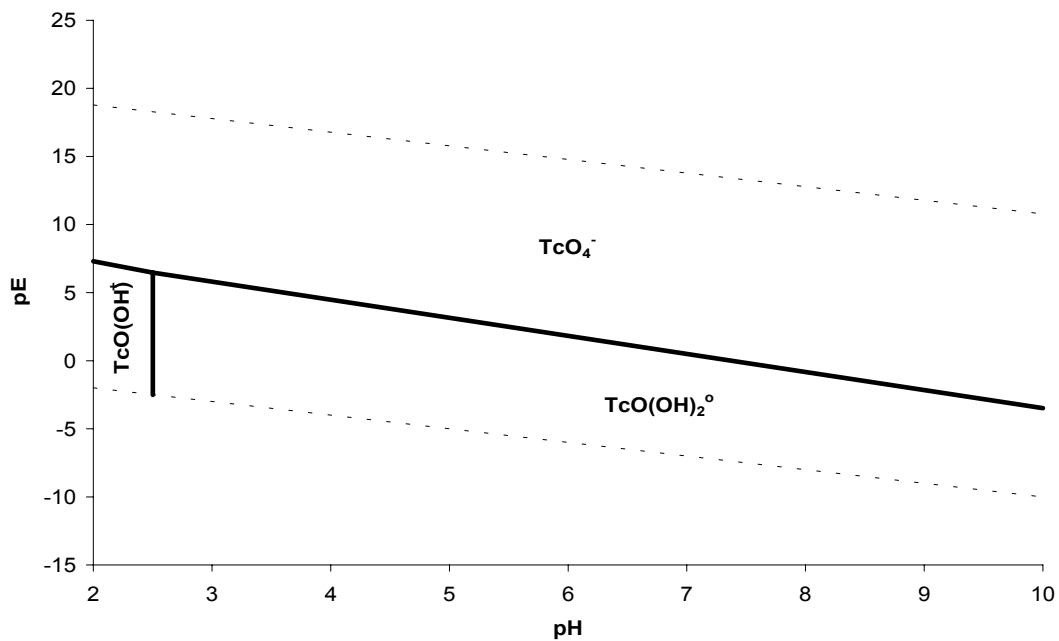
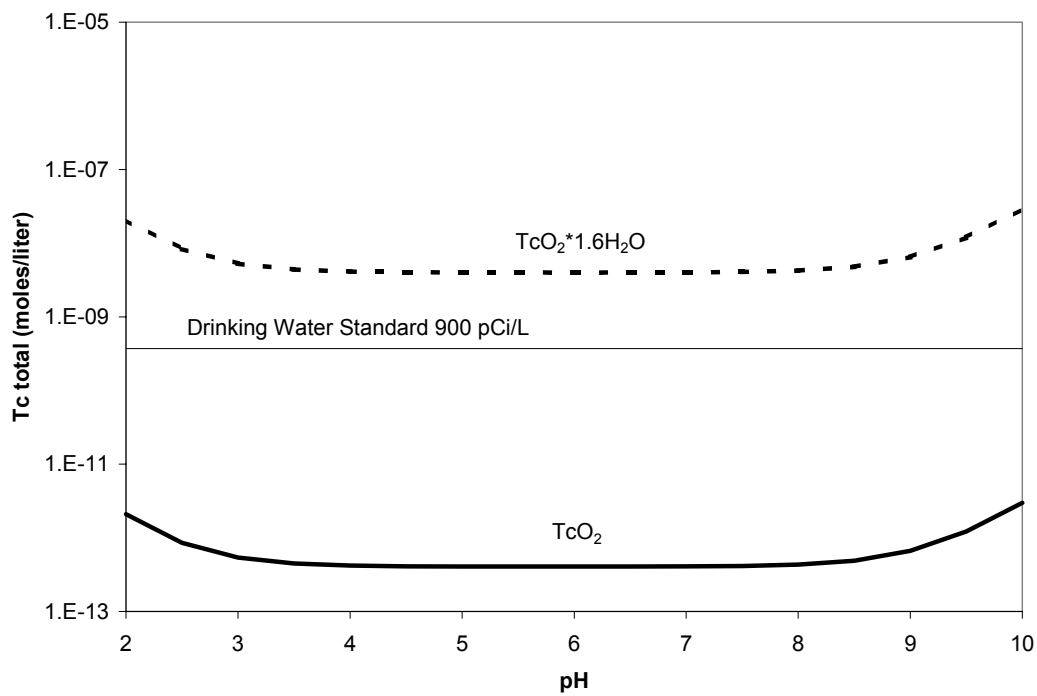**Figure 4. Speciation of dissolved technetium.**

Figure 5. Solubility of reduced technetium phases.

Amendments

Zero Valent Iron

Zero-valent iron is an effective amendment for contaminants that degrade or are stabilized by reducing conditions and high pH. The oxidation of zero-valent iron to ferrous iron is described by the half-cell:

$$Fe^o = Fe^{+2} + 2e- \qquad log\ K = 13.82$$

At a ferrous iron concentration of 0.1 mg/L the equilibrium pE is –9.8. This reduction potential is sufficient to reduce water to hydrogen gas and hydroxyl ions resulting in pH values that range from 9.8 to 12, depending on the composition of the solution.

Effectiveness: Zero valent iron can be an effective amendment for destruction of TCE, as well as stabilization of uranium and technetium. There is documented evidence for its effectiveness for all three contaminants (Gillham et al., 1993 *and numerous others for TCE*; Morrison et al, 2001; Morrison et al., 2002; Cantrell et al., 1995 *for uranium*; Liang, 1996; Korte, 1997 *for* ^{99}Tc). However, the elevated pH produced by zero valent iron (between 9.8 and 12) can actually reduce its effectiveness for uranium by the reaction:

$$UO_2 + OH- + 2H_2O = U(OH)_5^- \qquad log\ K = -5.83$$

Longevity: The effective lifetime of the amendment is shortened by the fact that zero valent iron produces the components that form coatings on the iron particles. In particular, ferrous hydroxide, ferrous carbonate, ferric hydroxide, and ferrous sulfide may contribute to coating the iron and reducing its life-time. Other coating phases will precipitate as hydroxides because of the elevated pH associated with zero valent iron. The rate that these coating phases precipitate depends on the composition of the groundwater. For example, elevated calcium concentrations in groundwater will result in additional coating phases of calcium carbonate and calcium hydroxide.

The longevity of the stabilization products of uranium and technetium depends on how fast the system returns to oxidizing conditions. This, in turn, depends on how rapidly coatings build-up on the iron. Once oxidizing conditions are re-established the reduced uranium and technetium phases will re-oxidize, releasing these constituents back into the groundwater.

Effluent Considerations: The effluent from a zero valent iron treatment system typically has a high pH and elevated ferrous iron concentrations. The effluent composition depends on exposure to the atmosphere because atmospheric gases (N_2, O_2, and CO_2) tend to buffer the reducing capacity of the iron. For example, equilibrium with atmospheric CO_2 lowers the equilibrium pH from 11 to 9 and elevates the equilibrium redox potential. At these conditions the stable form of nitrogen is N_2 rather than NH_3. If the system is not exposed to atmosphere, nitrate in the groundwater will be converted to NH_3. However, under these conditions, much of the ferrous iron will be precipitated as ferrous hydroxide and effluent concentrations will be lower.

Cost: Zero-valent iron costs about $550/ton. It should be noted that a ton of zero-valent iron is a much smaller volume than other amendments (0.1 m^3 for iron; 0.3 m^3 for apatite; 1.1 m^3 for peat)

Compatibility with Different Scenarios: Zero-valent iron is more compatible with a continuous flow scenario than with a batch scenario. Periodic exposure to atmosphere will hasten the coating process and reduce the longevity of the iron.

Peat

Many peat bogs form in areas that were originally small lakes and ponds. A typical bog formation process occurs over centuries. Vegetation spreads and fill the water body, and in some cases covers adjacent wetlands. As the peat accumulates, the bog remains saturated, except for a few inches on the top, where new growth occurs. Bog vegetation includes mosses, reed sedges, grasses, shrubs, and trees. Peat is gradually formed as the vegetation decomposes. Peat can be generally defined as a partially fossilized plant matter that occurs in wetlands where there is a deficiency in oxygen and where the accumulation of plant matter is faster than its decomposition. Peat is a complex material consisting of plant fibers that contain hemicellulose and cellulose, humic and fulvic acids, bitumens, waxes, resins, and other substances. As a result peat contains polar functional groups such as alcohol, aldehydes, ketones, and ethers that can be involved in chemical bonding and ion exchange. The polar and ion exchange functionality of peat has been shown to support sequestration of metals such as uranium and polar molecules such as ammonia. Peat also has a high surface area and high organic carbon content, similar to activated carbon, resulting in sequestration of organic contaminants (see information from www.peatec.com). Approximately 1.5 percent of the earth's surface is covered with peat, with the largest deposits occurring in the northern parts of the Northern Hemisphere. Canada, Russia and the former soviet republics account for approximately 80 percent of the total. In the United States, Alaska, Minnesota, Michigan and Wisconsin have the most extensive peat areas. Several of these areas provide abundant material for commercial applications.

In groundwater remediation systems peat can perform two functions. It acts as an absorbent for contaminants and promotes anaerobic/reducing conditions under which many contaminants are degraded or stabilized. Often, as with uranium (Nakashima et al., 1984), contaminants are initially adsorbed to peat and subsequently reduced to more stable forms. The adsorbent properties of peat for both organic and inorganic contaminants are well studied. Cohen et al. (1991) examined a variety of peats and found that all removed significant hydrocarbons from water. They concluded that organic adsorption properties were best in peats with low fiber and high ash content. Metals adsorb at the sites of carboxylic, phenolic, and hydroxylic functional groups (Gosset et al., 1986). Metal adsorption is strongly dependent on pH (Gosset et al., 1986) because H^+ competes with metal cations for adsorption sites. The optimum pH range for metal adsorption seems to be between 3.5 and 6.5 (Brown et al., 2000). At pH above 8.5 peat begins to degrade and metal sorption is decreased (Brown et al., 2000). The ability of peat to strongly adsorb a wide variety of contaminants makes it a common component of many wastewater treatment systems (Couillard, 1994; Brown et al., 2000).

Effectiveness: Peat can be moderately effective at promoting TCE degradation, as well as stabilization of uranium and technetium.

Peat sorbs TCE (increasing its residence time in the system for reactions to occur) and acts as a source of carbon and other nutrients to promote TCE biodegradation. Kao and Lei (2000) studied the use of peat as a biobarrier to degrade TCE and PCE. In a biobarrier inoculated with sludge, degradation of both solvents was rapid. They documented that peat slowly released the nutrients necessary to stimulate growth of bacteria provided by the sludge. Sheremata et al. (2000) showed that TCE was degraded to cis-1,2,-DCE up to 8 times faster in the presence of composted peat than in control experiments. A novel system tested by Kao and Borden (1997) used nutrient briquets to provide nitrate and phosphate followed by a peat barrier to provide a substrate for denitrification. Significant BTEX removal by this system was observed. Kao and Borden (1997) concluded that peat alone would not be an efficient method of remediating BTEX, but with the nutrient briquets peat does provide substantial bioremediation.

The potential for TCE degradation by peat at the WMU is high. The groundwater contains elevated concentrations of nitrate and a consortium of anaerobic bacteria from HRC injections. If phosphate were added to the system, all nutrients and bacteria necessary for reductive dechlorination of TCE would be present.

The reducing conditions sustained by peat would also promote stabilization of uranium and ^{99}Tc. Veselic et al. (2002) observed excellent uranium removal in two small-scale artificial wetlands. Morrison and Spangler (1992) demonstrated excellent uranium removal from water by peat, but concluded, based on redox measurements, that the uranium was predominantly sorbed rather than precipitated. However, if anaerobic conditions were prevalent in the peat it is likely that both uranium and technetium would be reduced to less soluble forms.

Longevity: Peat does not degrade rapidly as evidenced by its presence in the geologic record. However, its slow degradation does provide a continuous source of nutrients required to maintain reducing conditions. Gosset et al. (1986) found that the maximum adsorption capacity of unacidified peat for metals was about 200 mmol/kg (dry weight). However, adsorption capacity of peat can be enhanced by pretreatments (Couillard, 1994). Thus, peats longevity for adsorption depends on the peat used and site conditions.

The stabilized contaminants do have potential to be re-mobilized if the groundwater chemistry changes. However, as long as there is peat in the system and it is not exposed to the atmosphere, reducing conditions should be maintained. Likewise, sorbed contaminants should remain immobile if there are no major changes in the influent chemistry.

Effluent Considerations: Water coming out of a system with peat will have elevated chemical oxygen demand and a pH between 4 and 6. The reducing conditions will be sufficiently mild that N_2 will likely be the stable form of nitrogen. Thus, nitrate in the groundwater will not be converted to ammonia.

Cost: On a volume basis, peat is less expensive than other solid amendments.

Compatibility with different Scenarios: Operating a treatment system in a batch mode is less desirable than a continuous flow mode because of oxygen exposure issues. The

anaerobic microbial community maintains the reducing conditions in peat. Exposing this community to oxygen will diminish anaerobic microbial activity.

Solid Phosphate

Numerous studies have demonstrated that phosphate is an effective amendment for stabilization of many metals (examples: Gauglitz et al., 1992; Jeanjean et al., 1995; Ma *et al*., 1995; Zhang *et al*., 1997). The mechanisms for metal stabilization vary and include precipitation of contaminant metal phosphates, co-precipitation of contaminant metals in phosphate phases, adsorption onto phosphate minerals, enhanced adsorption to non-phosphate minerals, and biomineral precipitation.

Effectiveness: Stabilization of uranium may be achieved by any one of the above mechanisms. At high phosphate concentrations (>10 mg/L) autunite $[Ca(UO_2)_2(PO_4)_2]$ and other uranium phosphate phases may precipitate and effectively stabilize uranium (Gauglitz et al, 1992; Lee et al., 1995). For example, Jerden and Sinha (2003) observed U(VI) stabilization as a Ba meta-autunite. Groundwater associated with this deposit contained less than 15 ug/L uranium. At lower phosphate concentrations the solubility of uranyl phosphate phases will not constrain uranium concentration to below the Maximum Concentration Level (MCL) of 30 ug/L. However, uranium is known to co-precipitate with calcium or other metal phosphates. A natural example of this is the high concentrations of uranium (900 ppm) in the mineral gorceixite $[BaAl_3(PO_4)_2(OH)_5.H_2O]$ found in Aiken County, SC soils (Ferguson et al., 1979). The similar calcium phase, crandallite, is also known to contain elevated concentrations of uranium. These are low temperature weathering products that may precipitate when phosphate is added to soils. Finally, it has been observed that addition of phosphate stimulates microbial precipitation of uranium. Thomas and Macaskie (1996) found that microorganisms growing on tributyl phosphate effectively removed uranyl from water by precipitation of phosphate phases. Likewise, Roig et al. (1997) and Macaskie et al. (2000) concluded that a *Citrobacter* sp. accumulated uranyl when grown on glycerol 2-phosphate.

Phosphate can be added to a system in various forms. Apatite minerals are the most widely used solid amendments. They have relatively low solubilities as evidenced by their persistence in geologic environments. The advantage of this is amendment longevity, but the low solubility limits the amount of phosphate in solution. This, in turn, constrains precipitation of U(VI) to relatively high uranium concentrations. For example, Figure 1 suggests that at 2000 ug/L U(VI) and equilibrium with hydroxyapatite, phosphate phases are only likely to precipitate in a narrow pH range. Better performance has been reported for a form of apatite (Apatite II) made from fish bones (Conca and Wright, 2000). Alternatively, liquid phosphate solutions can be used to stabilize uranium. Liquid solutions have the advantage that much higher concentrations of dissolved phosphate can be maintained, and thus lower concentrations of uranium can be achieved. Experiments at the ACP demonstrated that solutions of $NaH_2PO_4:H_2O$ and phosphoric acid (H_3PO_4) were effective at stabilizing low uranium concentrations. These reagents were more effective than solutions of $Na_3PO_4:12H_2O$, perhaps because of the slightly higher pH produced by the trisodium phosphate. Tests were also done at the ACP on uranium stabilization by organic forms of phosphate, triethyl phosphate and tributyl phosphate. These were ineffective over the 21 day duration of the tests. Thomas and Macaskie (1996) found that uranium precipitation was coupled to biodegradation of tributyl phosphate, suggesting that microbial populations and time must be sufficient for organic forms of phosphate to stabilize uranium.

Longevity: Apatite minerals are persistent in the environment. The longevity of apatite amendments is more likely to be limited by coatings of precipitated phases or biofilms than by dissolution. Liquid phosphate solutions are not persistent, though inorganic phosphate can be expected to adsorb to other substrates and remain in a system for some time. However, if solutions of phosphate are used they will have to be replenished regularly.

The products of phosphate stabilization of U(VI) will be long-lived assuming the pH remains within there stable range. If stabilization is achieved by reduction of uranium, U(IV)-phosphate phases will dissolve as conditions return to oxidizing. However, if the pH is in the proper range, U(IV) phases may be replaced by U(VI)-phosphates in the presence of apatite.

Effluent Considerations: If pH is maintained near 7, phosphate concentrations from apatite will be approximately 15 mg/L. Liquid amendments are likely to generate higher phosphate concentrations at the effluent of a system. Depending upon other amendments used and PCO_2, the pH of effluent should be in the range of 6 to 8. Phosphoric acid generates a lower pH.

Cost: Hydroxyapatite ~ $250/ton
Apatite II ~ $500/ton
Solutions vary considerably depending on quality of reagent

Compatibility with Different Scenarios: Both liquid and solid phosphate amendments are compatible with continuous flow and batch scenarios.

Recommendations

shows a chart in which various aspects of potential amendments are evaluated. The only amendment that is effective for TCE, uranium, and 99Tc is zero-valent iron. However, zero-valent iron has serious effluent issues and we do not recommend its use at the WMU. Thus, we recommend a combination of peat and phosphate amendments.

Peat will adsorb TCE, uranium and technetium, but more importantly will provide a substrate for growth of anaerobic bacteria to maintain reducing conditions. Under these conditions TCE will be degraded by reductive dechlorination and uranium and technetium will be reduced to more stable forms. The phosphate amendment will help stabilize uranium, but also will provide an essential nutrient to promote anaerobic microbial growth. We recommend initial use of hydroxyapatite mixed with peat and sand. In addition, we recommend that provisions be made for injection of liquid phosphate or other nutrients into the treatment zone if needed.

Peat and phosphate are compatible (Table 2) and, in fact, are complementary. Phosphate provides an essential nutrient to maintain a robust microbial community. Phosphate adsorption onto peat may also enhance adsorption of uranium.

Table 1. Evaluation Matrix for Amendments.

KEY: ◉ ○ ●
better <------------> worse

Amendment	Effectiveness			Longevity		Outfall	Cost	Compatibility with Scenarios	
	TCE	Uranium	Tc-99	Amendment	Product			Batch	Continuous
Zero Valent Iron	◉	○	◉	●	●	●	○	●	◉
Solid Phosphate	●	◉	●	◉	◉	◉	○	◉	◉
Liquid Phosphate	●	◉	●	◉	◉	◉	○	◉	◉
Peat	○	○	○	◉	○	◉	◉	○	◉
Liquid Organic	◉	◉	○	●	●	◉	○	○	◉
HRC	◉	○	○	●	●	○	●	○	◉
MRC	◉	○	○	●	●	○	●	○	◉
ORC	◉	●	●	●	NA	◉	●	◉	◉

DEFINITIONS / NOTES:

Effectiveness
◉ = demonstrated effectiveness
○ = theoretical basis for benefit
● = no known benefit

Amendment Longevity
◉ = may last indefinitely
● = probable longevity of months to <5 years

Product Longevity
◉ = forms a phase that is stable under natural conditions
○ = a combination of meta-stable phases and cation exchange
● = forms phases that are not stable under natural conditions
NA = not applicable because there is no product

Outfall
◉ = low potential to violate limits
○ = intermediate potential to violate limits
● = high potential to violate limits

Cost
◉ = low cost per volume
○ = intermediate cost per volume
● = high cost per volume

passive treatment
◉ = system is fairly compatible with passive operations such as peat beds, wetlands, treatment ponds, etc.
○ = generally compatible but may not be optimal due to high flow rate or cycled operation

Table 2. Compatibility Matrix for Amendments.

KEY: ◉   ○   ●
       better <------------> worse

Amendment	Zero Valent Iron	Solid Phosphate	Liquid Phosphate	Peat	Liquid Organic	HRC	MRC	ORC
Zero Valent Iron	–	●	●	○	X	X	X	X
Solid Phosphate	●	–	X	◉	◉	◉	◉	◉
Liquid Phosphate	●	X	–	◉	◉	◉	◉	◉
Peat	○	◉	◉	–	X	X	X	X
Liquid Organic	X	◉	◉	X	–	X	X	X
HRC	X	◉	◉	X	X	–	X	X
MRC	X	◉	◉	X	X	X	–	X
ORC	X	◉	◉	X	X	X	X	–

Excavation Based Groundwater Plume Treatment Options

As noted in DOE (2002), targeted removal of the source by excavation provides several significant opportunities. In particular, the robust subsurface access afforded by the excavation provides and opportunity for beneficial transition to a relatively effective system for hydraulic control, plume capture, and possibly for passive or *in situ* treatment. These thoughts were highlighted in previous independent technical assistance recommendations for this site:

> "AEMP should also consider using existing infrastructure (e.g., storm sewer line removals and source excavation area) to help in setting up a stable and sustainable remediation system. Steps should be taken to accelerate …{source removal and AEMP should consider discontinuing}… HRC injection …{if it is ineffective in meeting goals and schedules}. Excavation will remove Tc-99 and most of the TCE and U source terms. The TCE in the excavated material could be quickly removed while in a staging area using desorption techniques like SVE. This would allow the material to be ...{disposed as LLRW under appropriate conditions}." (DOE, 2002)

Figure 6 is a simplified schematic of the recommended conceptual approach. There is a significant potential for use of any excavation to enhance remediation efforts by:

> "…installing a high permeability backfill material to facilitate controlled drainage, possibly including amendments such as reducing agents and/or a phosphate source. Transitioning to monitored natural attenuation for long-term strategy should be considered. The site could also consider drilling a down gradient drain or a geosiphon … from the bottom of the excavation. This could be supplemented as needed by lateral horizontal wells or drains. See Figure 6 for details. If monitoring data indicates a need, ACP should consider amendments to reduce residual on-site groundwater contamination levels to allow license termination. Then the site should transition to MNA as rapidly as possible given the constraints of a thorough risk assessment with more relevant targets for groundwater for both TCE and U." (DOE, 2002)

Successfully transitioning these concepts into practice in such a way that provides maximum potential benefits requires careful analysis. Currently, source excavation, followed by installation of a geodrain (amended to provide treatment and stabilization) in the baseline technology. A period of ex situ treatment is included as a contingency until data indicate that the amendments are effective. This report uses the terminology "excavation based treatment" for those systems that utilize a source excavation and a central feature of the follow-on groundwater treatment phase and "other alternatives" for systems that do not rely on an initial large-scale excavation. Final selection and implementation of excavation based treatment, or alternative nonexcavation based treatment, requires evaluation of hydrological, geochemical, and risk factors and the blending and balancing of the results of the various analyses.
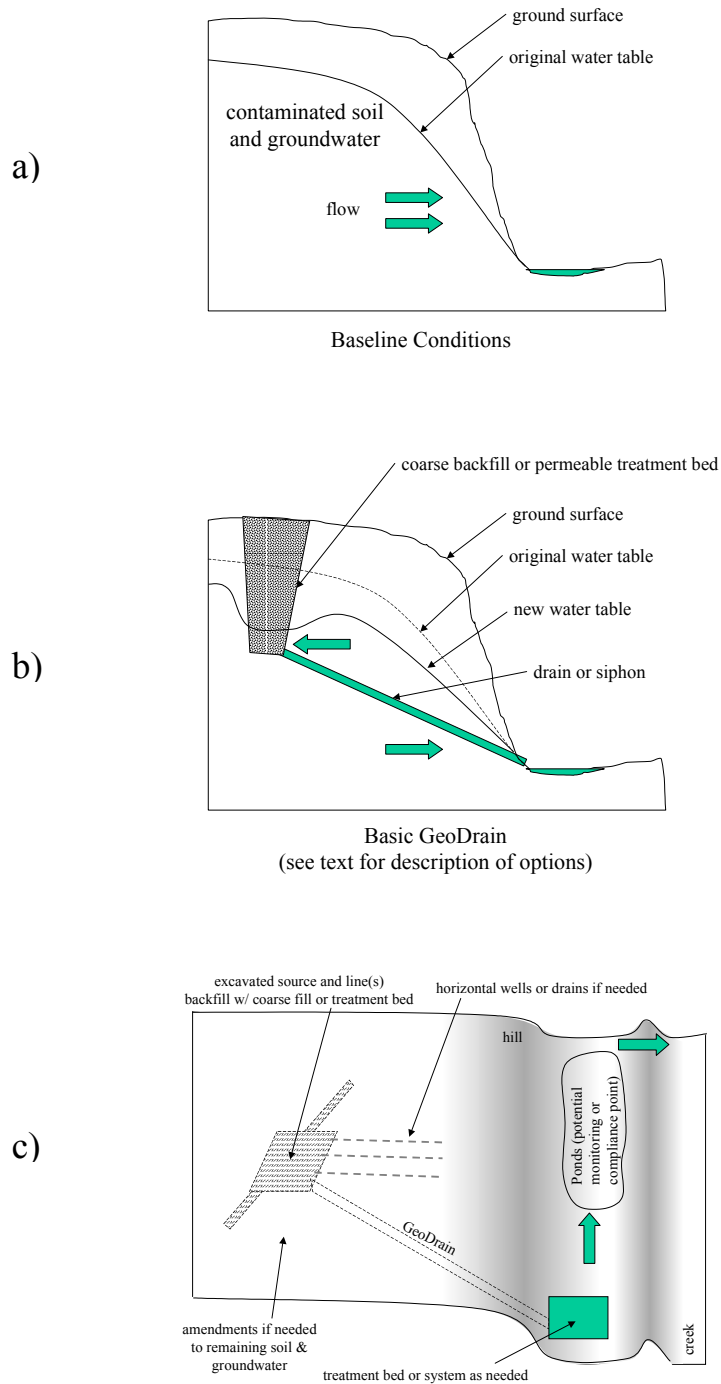
Figure 6. Simplified Schematic Diagrams of WMU and Groundwater Options for - a) baseline conditions, b) cross section, c) site configuration.

Hydrology and Configuration Considerations Following Excavation

A key to implementing an integrated source removal groundwater management approach is: 1) weighing the pluses and minuses of various post excavation configuration options and then 2) selecting from those that have the potential for the best performance in terms of flow/capture, flexibility, reliability and cost effectiveness. The approximate total flow captured by the excavation is an important system constraint that will factor in to the evaluation. Calculation of the approximate flow rate of water entering an excavation is documented in the construction dewatering literature (see, Powers, 1981). For the ACP excavation a simplified diagram can be constructed that defines some of the terms in the calculation (Figure 7). In this diagram, R is the radius of influence -- the distance at which there is minimal drawdown caused by the excavation. The distances for R are measured from the center of the excavation and thus R at time zero is, by definition, the radius of the excavation itself and R increases thereafter as water flows into the excavation. The estimated flow rate is fastest immediately after the excavation is made (since the gradient is steep) and slows down over time as the water levels drop and the radius of influence increases. It is important to note that this approach is only an approximation that is based on many simplifications. Further, the methods are less reliable for excavations in low permeability systems (where small preferential flow paths can dominate flows). Nonetheless, the method is a useful tool for projecting flows to compare alternative configurations. Using the nomenclature in Figure 7, the following basic equations are often used to approximate flow and radius of influence (Powers 1981):

$$Q_t = \pi K \, (H^2 - h^2) \, / \, \ln(R_{0,t} \, / \, r_s)$$

$$R_{0,t} = r_s + \sqrt{(T * \text{time}) \, / \, C_s}$$

In these equations, all terms must be converted to consistent units (e.g., length in meters, time in seconds) and the results (e.g., m^3/sec) then converted as needed to other engineering units (e.g., gpm). For an excavation approximately equivalent to the source removal at Ashtabula and for typical Ashtabula hydraulic conductivity (see Appendix A), the resulting flow rate and radius of influence are shown in Figure 8 and Figure 9, respectively.

A striking feature of the cursory hydraulic analysis is the relatively low flow rates generated in this system for a deep excavation installed relatively deeply into the water table aquifer. While initial flow rates are relatively high (in the range of 0.6 to 19 gpm after one day), the flow rate drops off as the nearby water table is drained. Flow rates after a year are estimated to be in the 0.05 to 1.25 gpm range and after 10 years in the 0.02 to 0.6 gpm range. The drawdown curve is steep and the estimated radius of influence grows slowly (since the hydraulic conductivity is low) eventually reaching values in the range of about 80 to 250 feet after ten years. These results suggest that it will be crucial to long term success to develop a treatment approach that is logical for a low flow rate and to incorporate design features to increase flows and radius of influence to the extent practical.

$R_{0,t}$

r_s

excavation

initial water level

drawdown = H - h

H

b

h

a)

K = hydraulic conductivity
T = transmissivity = Kb
C_s = coefficient of storage

excavation

$r_s = R_{0,0}$

Q_0

Q_{t1}

$R_{0,t1}$

Q_{t2}

Q_{t3}

$R_{0,t2}$

$R_{0,t3}$

b)
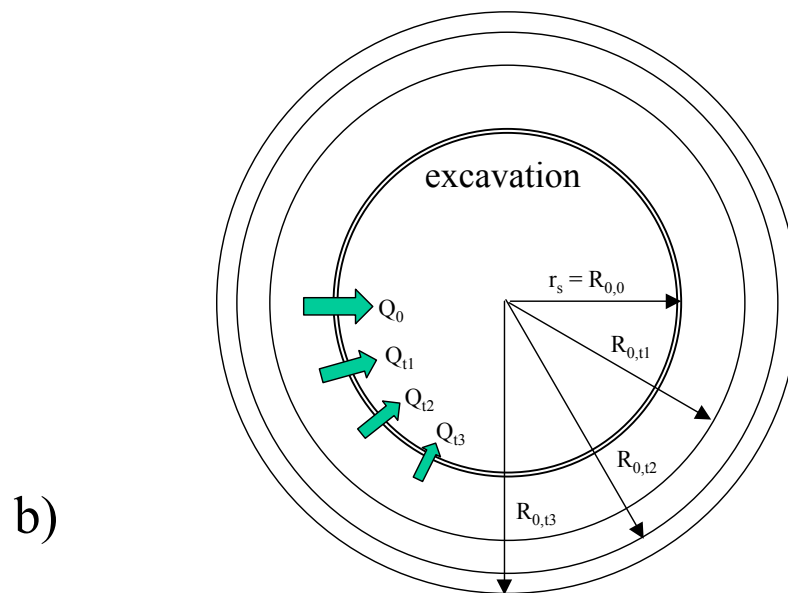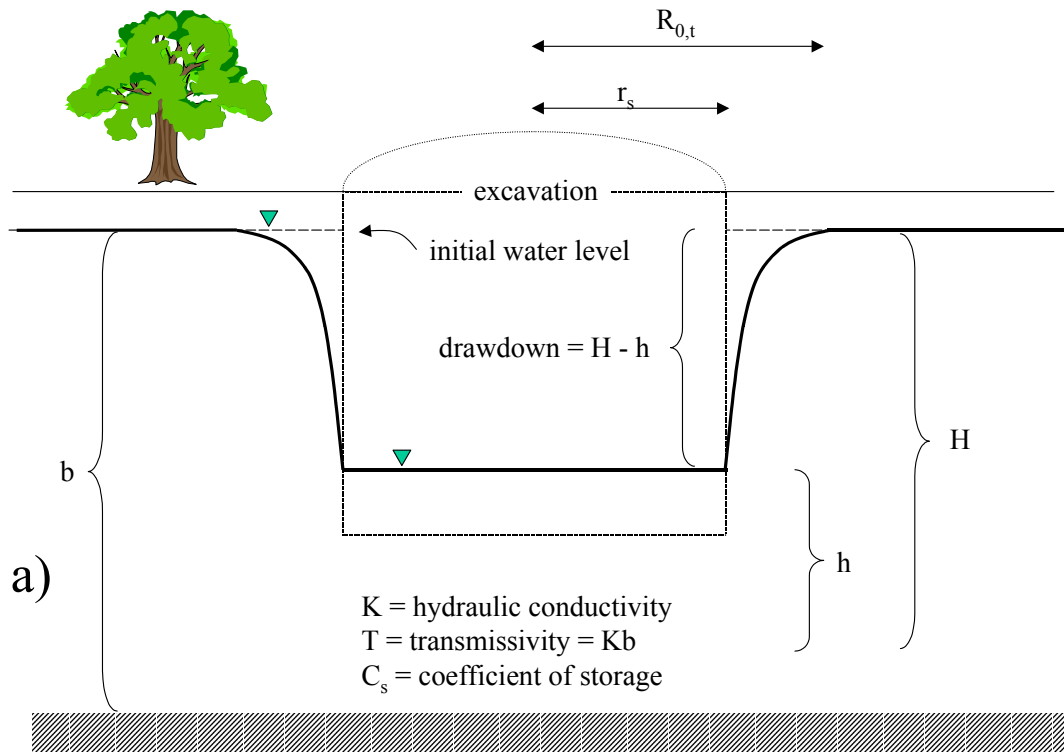
where
$R_{0,i}$ = approximate radius of influence at times 0, t1, t2 and t3
Q_i = approximate flow at times 0, t1, t2 and t3

Figure 7. Simplified excavation and hydrologic analysis diagram – a) cross section and b) plan view.

Flow from passive capture system as a function of time
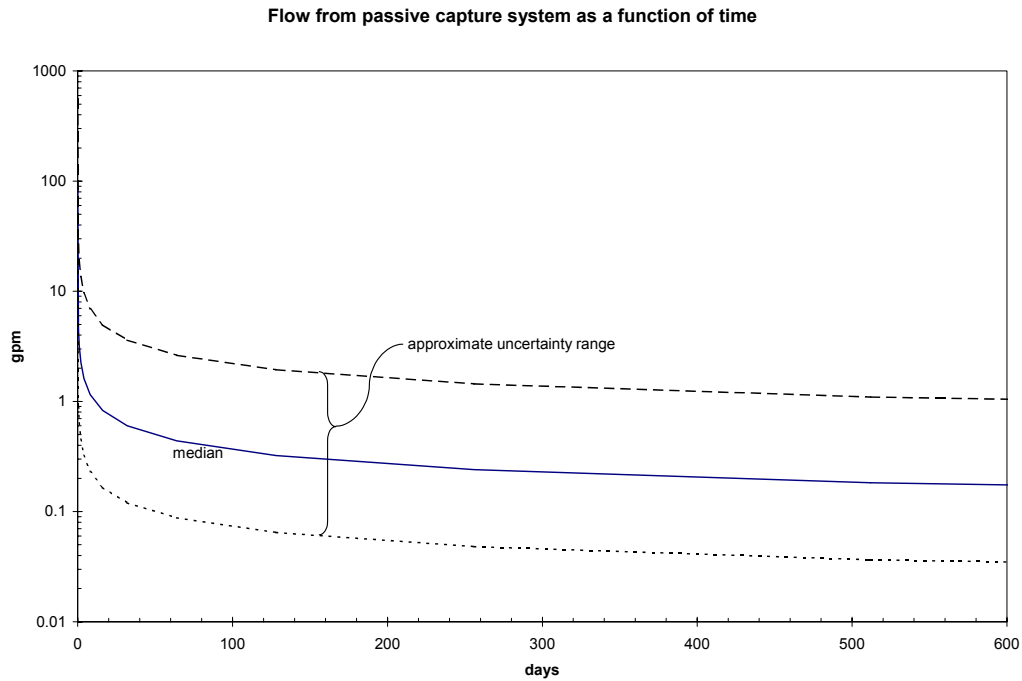
Figure 8. Expected flow – uncertainty range based on hydraulic conductivity.

Approximate radius of influence
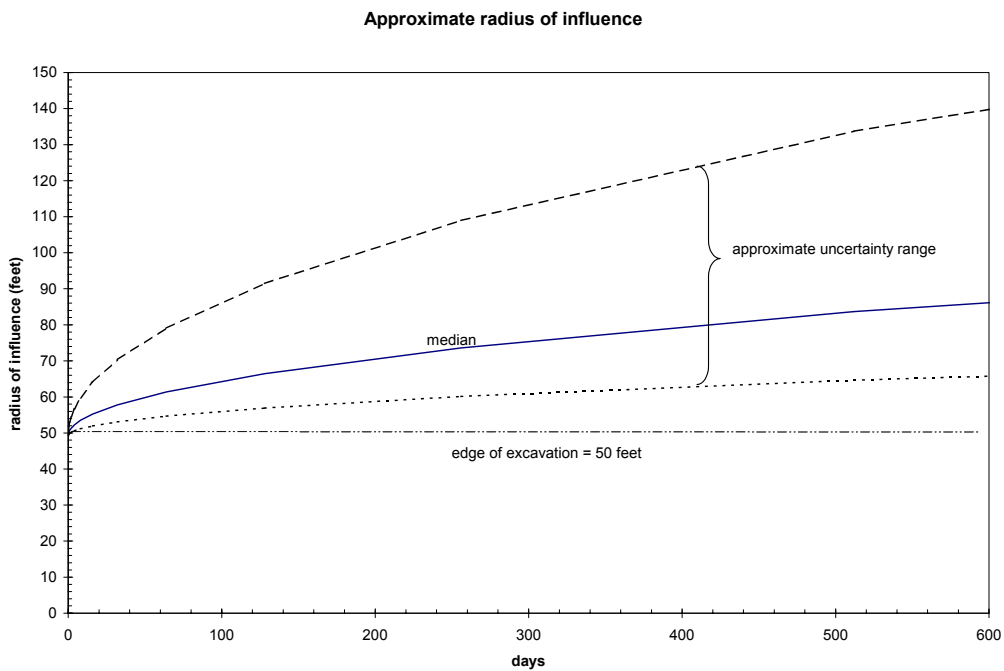
Figure 9. Expected radius of influence – uncertainty range based on hydraulic conductivity.

Based on the relatively low flow rates calculated, the original (DOE, 2002) recommendation for incorporating horizontal drains and other design features to extend the zone of influence and increase flow may, be appropriate. Importantly, these horizontal drains (if necessary) should focus on the upper oxidized brown till (higher permeability strata) and would have minimal benefit in the deeper gray clay (lower permeability strata). Additionally, the potential for low flow has some specific ramifications related to operating paradigms and the incorporation of *in situ* treatment/stabilization amendments. Note that a relatively modest drawdown was assumed in the initial hydraulic evaluation (a requirement of the analysis approach) and somewhat higher flow rates would result from maximizing drawdown. This tradeoff between flow and drawdown is a good example of the balancing required in design – low water levels maximize flow rate but provide a limited zone for amendments (the dry portion of the backfill will not participate in treatment or stabilization). This simple example suggests evaluation of the advantages and disadvantages of alternate configurations (e.g., batch versus continuous) and operating approaches (water level control, and the like) for the hydraulic capture and treatment system. These are summarized below:

- Continuous or batch flow in combination with ex situ treatment – continuous flow systems can be implemented using a fixed design to maintain a low or moderate water level or can be implemented using a manual control or pump system to allow alternative water levels to be optimized. Batch flow systems allow the water level to cycle through a range and can be implemented using a manual control or pump system, or using a passive control system similar to a laboratory pipette washer. Ex situ treatment can be implemented using traditional unit operations such as air sparging and ion exchange, or using passive treatment such as a wetland, a peat bed, or pool-cascade system. (increasing the potential contact with amendments and increasing contact time).

- Continuous or batch flow in combination with *in situ* treatment – as above, continuous flow systems can be implemented using a fixed design to maintain a low or moderate water level or can be implemented using a manual control or pump system. The water level maintained in the system will significantly impact the effectiveness of the amendments. Batch flow systems allow the water level to cycle through a range (potentially increasing the contact with amendments and increasing contact/reaction time) and can be implemented as described above.

- Backfill excavation with low permeability fill and without geodrain (no flow). This option includes both backfill of large scale excavation without flow and hot spot removal of the TCE source (assuming radionuclides meet soil criteria).

Figure 10 depicts the continuous flow system. Figure 11 depicts a batch flow system that uses manual control. Figure 12 depicts a batch system that uses passive control – the pipette washer. Each figure summarizes control and treatment options and issues. Table 3 provides a summary analysis of the various configurations by assessing the relative performance of the configuration using a variety of criteria.
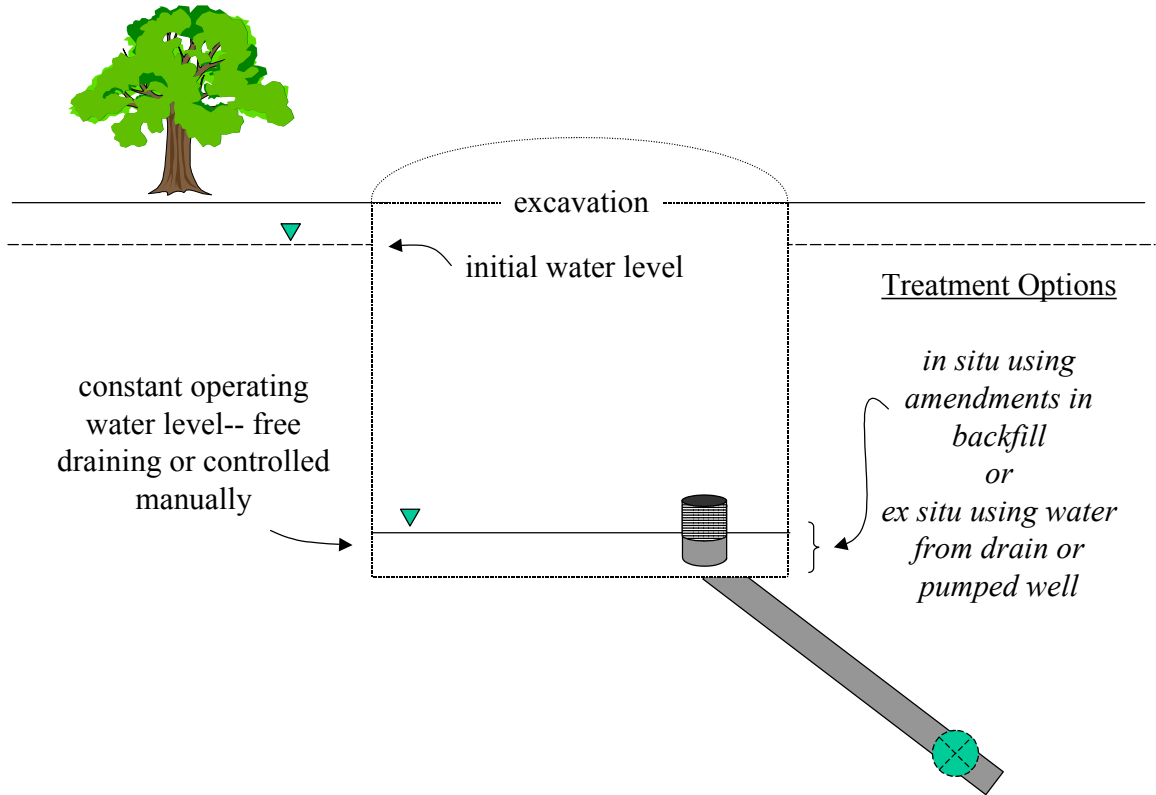
Figure 10. Continuous Flow System.
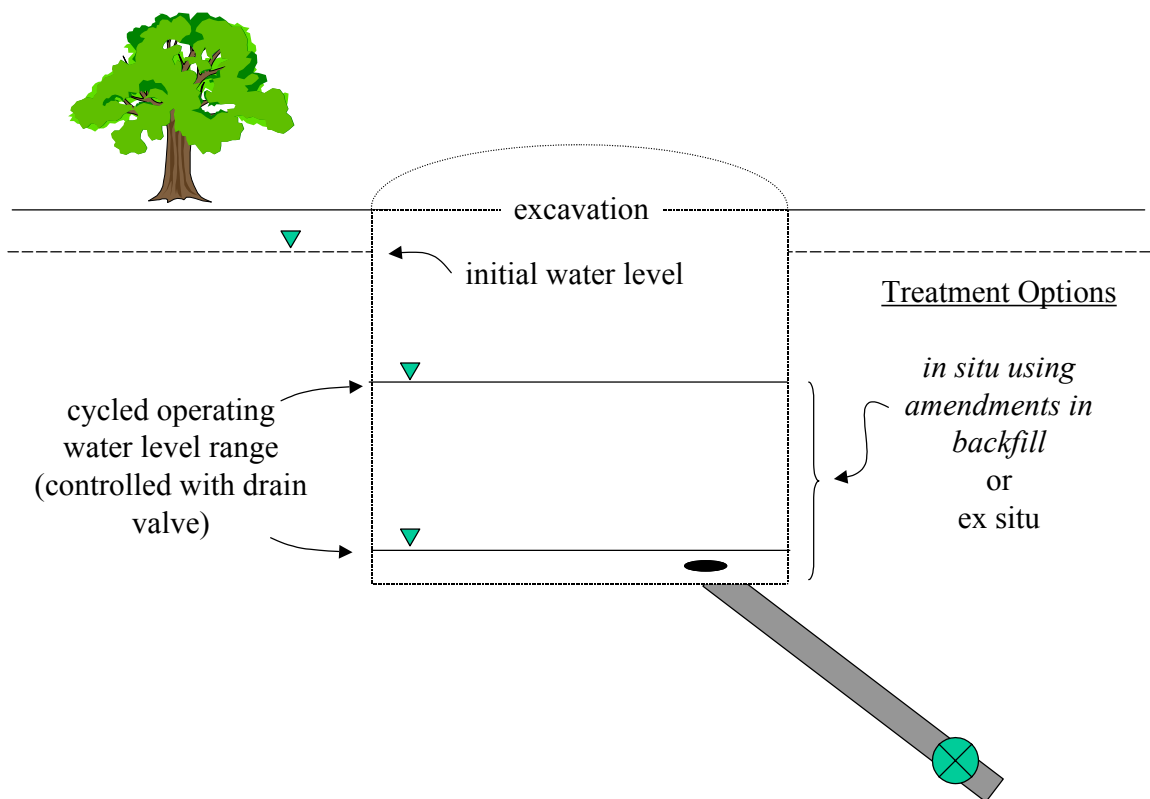
Figure 11. Batch flow system with manual control.
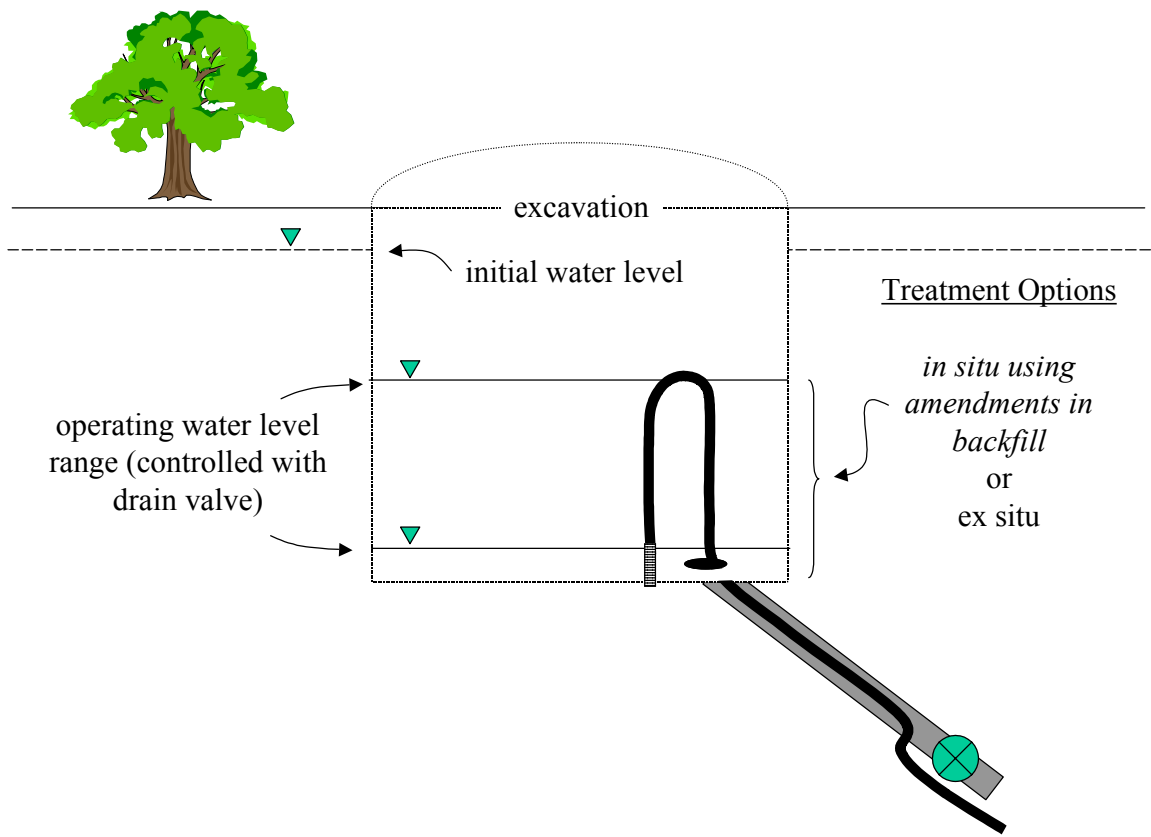
Figure 12. Batch flow system with passive control similar to laboratory pipette washer.

Table 3. **Summary Evaluation of General Configuration Options.**

Qualitative evaluation of various configuration concepts for capturing and treating water after targeted excavation of source material

KEY: ◉   ○   ●
better   <-------------->   worse

Treatment Option	Hydrology and Engineering Factors			In Situ Treatment Factors		Ex situ treatment Factors	
	water level during operation	relative flow rate	flexibility	amendment thickness and quantity	reaction time	traditional water treatment	passive
Continuous Flow	low	◉	●	●	●	◉	○
Continuous Flow	medium	●	●	○	○	○	◉
Continuous Flow	manual level control	● / ○	◉	○	○	○	◉
Batch Flow (manual)	cycled	○	◉	○	◉	○	○
Batch Flow (passive)	cycled	○	◉	○	◉	●	○
No Flow	na =not applicable	●	●	na	na	na	na

DEFINITIONS / NOTES:

relative flow rate:
◉ = highest relative flow rate assuming drainage to large excavation and maintaining maximum drawdown
○ = intermediate flow based on cycling between moderate and maximum drawdown
● = lowest relative flow based on continuously maintianing moderate drawdown

flexibility:
◉ = flexible and easily reconfigured to respond to performance monitoring information
○ = intermediate flexibility
● = minimal options for responding to reconfiguration needs
note that configuration for manual and cycled systems is almost identical and the resulting systems can be operated in either mode.

amendment thickness & quantity:
○ = entire zone between bottom of excavation and intermediate nominal water level available for amendment
● = minimal thickness near bottom of excavation available for amendment

reaction time
◉ = longer reaction time possible due to batch operation
○ = intermediate
● = minimal reaction time due to minimal amendment thickness, relatively fast flow etc.

traditional water treatment:
◉ = system is fairly compatible with traditional unit operations such as ion exchange and air stripping
○ = generally compatible but may not be optimal due to low flow rate or cycled operation
● = poor match to traditional treatment because cycled operation and limited control of timing of cycles

passive treatment
◉ = system is fairly compatible with passive operations such as peat beds, wetlands, treatment ponds, etc.
○ = generally compatible but may not be optimal due to high flow rate or cycled operation

"No Flow" would be excavation and backfill with no geodrain and would also include TCE source hot spot removal with no flow system implemented. This option would likely be combined with other plume treatment and containment strategies where the use of amendments and flow controls would be more expensive or where the production of water over time is undesirable.

As noted in the construction dewatering calculations, the flow rate from the system after the initial influx of water would be expected to fall roughly into the range of 0.1 to 1 gpm. Continuous flow systems that maintain a maximum drawdown would maximize flow and perhaps yield flows somewhat higher than this range. Batch systems could be operated to have an average water level similar to that assumed in the calculation and thus yield water volumes equivalent to the calculated flow rates. Based on a rough batch treatment volume of 300,000 gallons the flow rates suggests that batch treatment times would range from 200 days to 2000 days. Even if the system exhibits significant heterogeneity that increases flow rates by an order of magnitude, batch treatment times greater than 1 month are likely in this system. The calculated batch intervals are relatively long and may provide useful reaction time for amendments.

Related Hydrologic Issues

Maximum effectiveness of the excavation based capture system may be realized if infiltration and other sources of water to the system are minimized. Each gallon of water that is diverted from of the subsurface system results in an equivalent reduction in the

plume migration and potential discharge. Thus, when the excavation process is completed, the site should be configured to shed water and minimize infiltration. This does not necessarily require a cap, but simply that the minimization of infiltration be a factor in the design process. Similarly, there is great potential benefit in performing an engineering analysis of anthropogenic sources of water (leaking domestic, process, and fire water lines) and taking any cost effective actions that would reduce the contribution(s) of water that these sources make to the subsurface.

Excavation with Impermeable Backfill as an Alternative to the Geodrain

Excavation of contaminated material and backfill with an impermeable material is a proven technology that will directly reduce the source (by excavation) and then minimize the spread of contaminants (by reducing the flow through permeable lenses adjacent to the source and hydraulic isolation). This concept does not employ a geodrain and, thus, has the benefit of not generating a waste stream requiring treatment. The trade off is that the hydraulic controls rely on plugging the system rather than on inducing a strong flow back toward the center of the plume to control plume growth. The excavation and backfill benefits are insensitive to the nature of the contaminant – working equally well for TCE, uranium and technetium. Possible implementation scenarios include:

1. Excavation/offsite disposal of contaminated material (under excavation-based baseline) followed by grading and/or backfill with impermeable fill. Uses source control and containment.
2. Excavation w/o disposal; grading/backfill of excavated material amended with additional stabilizing agents as necessary to make backfill impermeable. Containment only.

Several factors influence implementation:

*   *Ground Water Issues Remain After Soil Source Remediation:* Under Excavation/Disposal-based approaches, excavation and offsite disposal of contaminated soils will meet cleanup standards for soil. This approach will effectively provide source control for all contaminants to the negotiated cleanup levels for soil. The excavations will have to be backfilled (or regraded, at a minimum). However, under even the most conservative soil standard, residual groundwater contamination at levels above groundwater standards (e.g., MCLs) is expected to remain after excavation; hence need for follow-on groundwater treatment. Other approaches to address remaining groundwater contamination are likely to take years to meet standards whether using an active or a passive approach. Thus, some sort of groundwater containment strategy is desirable. Installing an appropriate backfill to provide plugging and isolation within the central high concentration areas of the plume is a simple and low cost form of partial containment that may be useful in combination with other plume treatment and containment strategies.

*   *Results of Blending Site Soils:* Results of the recent ACP utility line investigation showed that when native materials are excavated and then returned to the excavation as backfill, the silt stringers that previously served as conduits are destroyed and this conduit path is interrupted and largely eliminated. Excavation of contaminated soils with silt stringers, followed by homogenization and backfill will result in a reduction of the of water and contaminant migration. If blending

does not generate a low-enough permeability material, amendments could be added.

- *Sources of Impermeable Materials: Historic* cleanup operations have generated several piles of low-permeability soils suitable for use as site backfill. These could be blended with newly-excavated soils, amended as needed to meet permeability goals, and returned to the excavation at low cost.   The site could balance cuts from non-affected areas with fills.

"Other" Groundwater Plume Remediation Approaches

In Situ **Bioremediation**

Anaerobic bioremediation is a well-proven technology in which anaerobic microorganisms degrade chlorinated solvents by the mechanism of reductive dehalogenation (Figure 13). The pathway for this mechanism includes the degradation intermediates dichloroethene, vinyl chloride and ethene. There is data from groundwater wells at the site in recent history that these degradation products were present. This microbial activity requires strongly anaerobic conditions and the presence of anaerobic microorganisms possessing reductive dehalogenation capability. In cases where natural conditions do not support active anaerobic reductive dehalogenation, it is common to deploy biostimulation (addition of carbon sources to produce anaerobic conditions) as well as bioaugmentation (addition of anaerobic halorespiring bacteria) to achieve *in situ* anaerobic biodegradation of chlorinated solvents. Correct conditions and the presence of appropriate biocatalysts will commonly result in complete degradation of chlorinated solvents.
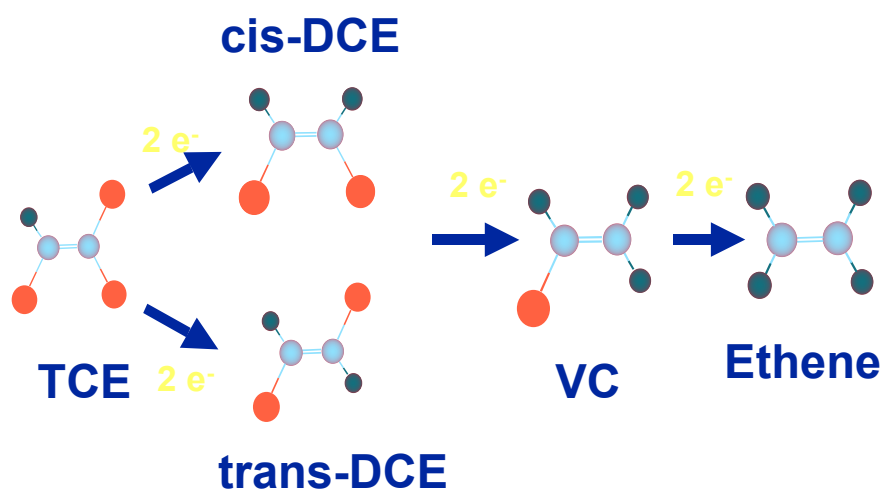
Figure 13. Pathway for stepwise reductive dechlorination of Trichloroethylene.

Application of anaerobic bioremediation for *in situ* treatment of contaminated soils at the ACP site would require that strong anaerobic conditions be established and maintained. This could be done by exclusion of oxygen, but more likely by biostimulation with excess organic nutrient supplementation. Because halorespiring bacteria can use chlorinated ethenes as terminal electron acceptors in order to gain energy, the environment must first be depleted of all other potential terminal electron acceptors with higher energy levels, eg. nitrate and sulfate (Figure 14). The halorespirers like *Dehalococcoides ethogenes* are one of the few organisms that degrade Tetrachloroethylene(PCE) and TCE all the way to ethene, via stepwise reductive dechlorination (Figure 13) . However, some sites are known to go into what is referred to as a 'stall' where reductive dechlorination stops at either cis-DCE or vinyl chloride. Usually this stall is caused by lack of halorespirers, or high concentrations of competing terminal electron acceptors. Additionally, the bioprocess conditions would need to be held within acceptable ranges for temperature, pH, and moisture. Macronutrient additions (primarily nitrogen and phosphorous) may also be required. For *in situ* biostimulation at the WMU in the source area the greatest problem will be the low permeability of the soil. Hydraulic conductivities of 10^{-4}-10^{-7} cm/sec are minimally acceptable for any type of liquid injection. However, *in situ* stimulation of bioreduction has the added advantage of being capable of reducing U, and making it less soluble and hence stabilizing it *in situ*. The effectiveness of biostabilization strategies for U have an uncertainty as to their long-term stability and their effectiveness under normal environmental conditions, though laboratory studies show great promise. If the normal site condition becomes or is reducing than this may not be an important issue. Currently it is unclear what the normal condition is, since the same well can have undetectable concentrations of oxygen or 2-4 ppm DO in just 24-48 hours.

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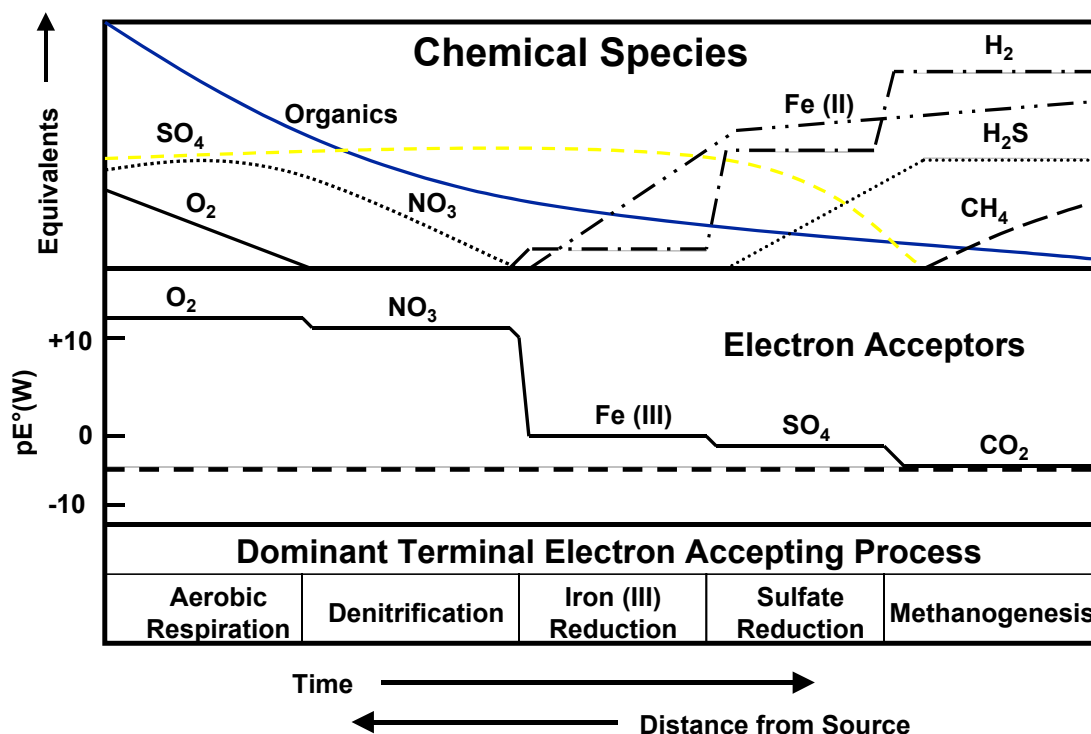
Figure 14. Critical chemical species, electron acceptors, and redox processes in relationship to bounding conditions necessary for reductive dechlorination of TCE (dashed line).

A number of carbon compounds can act as electron donors to drive anaerobic processes, for more discussion see the section below on carbon amendments. Because RMIES has already used HRC, and lactate is a proven product for both TCE and U reduction, we will confine our discussion to lactate as the electron donor of *in situ* bioremediation in this case. The mechanism is similar for all of the potential carbon sources that could be used, but none are as simple as lactate. HRC (hydrogen release compound) has already been injected at the site and was a good choice as an electron donor for biostimulation of indigenous microbes. HRC is a polylactate compound that slowly releases lactate when mixed with water (Figure 15). The released lactic acid stimulates both aerobic and anaerobic microbes by providing a carbon and energy source. Anaerobic microbes ferment the lactic acid into pyruvic acid and then to acetic acid, releasing 2 moles of molecular hydrogen per mole of lactate. Investigations conducted by Regenesis, Ltd. showed that the slow release characteristics of HRC cause reducing conditions to be maintained for a long time (up to 18 months) with a single HRC application. This is a cost effective aquifer treatment as compared to other remediation technologies, in aquifers where it is applicable and time is not a constraint.
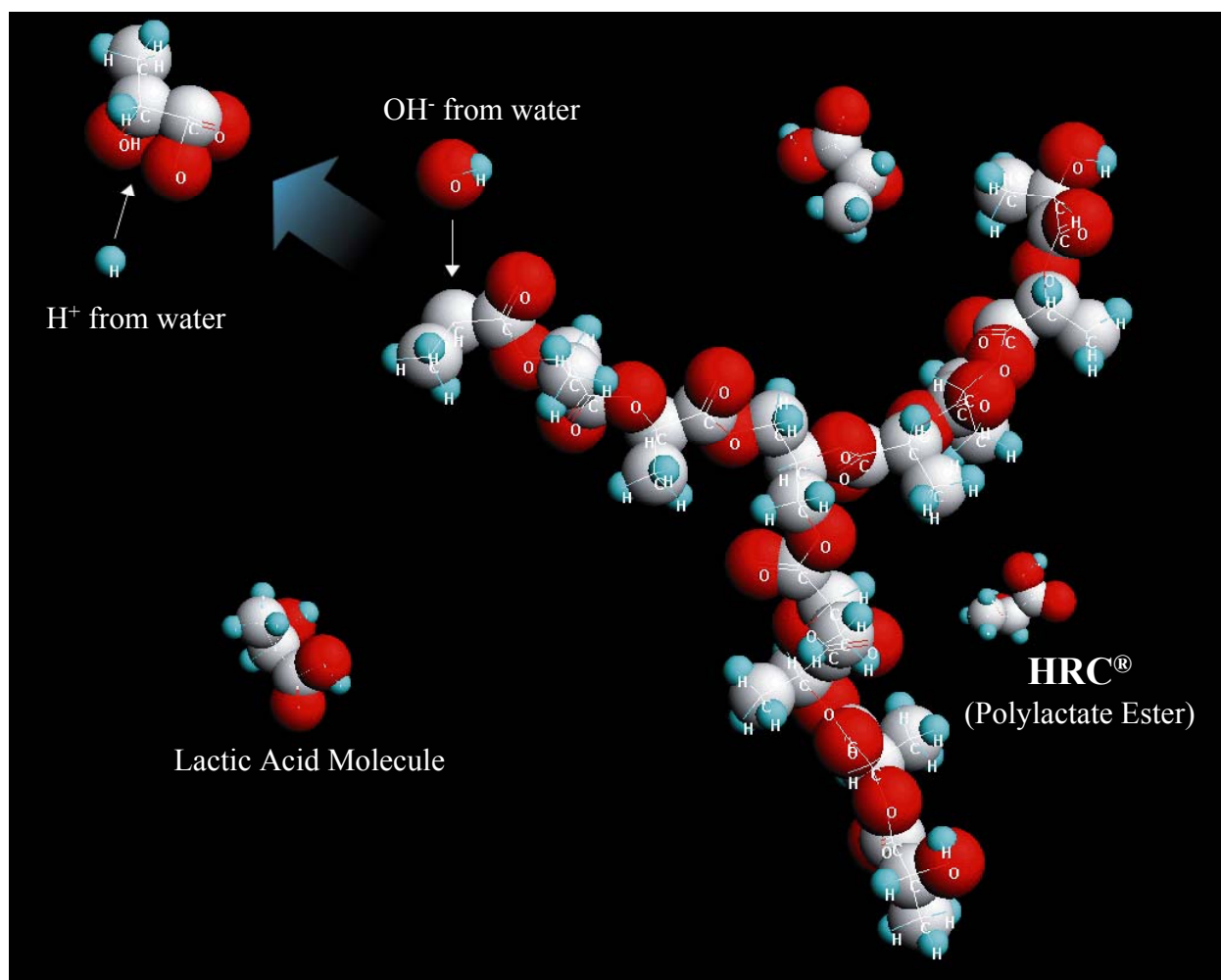
Figure 15. The polylactate ester structure of HRC and it's solubilization in water.

Since it is possible that indigenous microbial populations under anaerobic conditions may not degrade chlorinated solvents or only partially degrade them. The past detection of undegraded chlorinated solvent intermediates (e. g., cis-DCE and vinyl chloride) in groundwater at the ACP site indicates this may be problematic. Partial microbial degradation could result in significant production of degradation intermediates that have a significant lower WAC than the original chlorinated solvent(s). Anaerobic microorganisms typically grow slowly and the time required to get to a reasonable cleanup goal could be excessive.

During implementation of the bioremediation project, a contingency was developed to address problems regarding the buildup of intermediates such as cis-DCE and vinyl chloride. SEC and Regenesis believe it is very unlikely that any buildup will occur based on previous experience in similar geologies. However, they did include a contingency to utilize Oxygen Release Compound (ORC) to force the system aerobic and promote the rapid breakdown of the intermediates *in situ,* if necessary. This contingency has similar

problems with HRC in that it requires injection material into a low hydraulic conductivity environment. The aerobic conditions would also be subject to the same nutrient limitations as the anaerobic environment. In addition, the effect of reduction of the U to less soluble states would be reversed, and thus increasing the mobility of the U into the groundwater.

The site injected 24,730 lbs of HRC around and in the WMU from April to May 2002. Subsequently groundwater was sampled baseline and quarterly until December 2002 and sediment was sampled baseline and in December 2002. The goal of this source remediation was 65% annual reduction with overall 95-98% reduction after 3 years. The soil sampling indicated that there was more than 1,738 lbs of TCE vs. the 658 lbs. that was originally thought to be present. In addition, the nitrate concentrations were predicted to be about 40 ppm, but the actual average concentration was 1504 ppm. The dissolved oxygen concentration was also higher in the groundwater then predicted, though this data is suspect. This immediately suggests that the amount of HRC required to deplete the nitrate and to degrade the TCE would be much greater. The TOC measurements from the groundwater were all below 100 ppm, which would indicate that the amount of electron donor was insufficient to achieve anaerobic conditions (Figure 14).

The water data suggest that there were slightly higher concentrations of TCE during the first 2 quarters and slighter lower concentrations of TCE in some wells during the 3rd quarter. This phenomena is typical since it would take some time for the stimulated bacteria to deplete the competing electron acceptors and increased solubilization from the HRC addition and increased microbial activity (biosurfactants) would release more sorbed TCE from the soil into the groundwater. Though cis-DCE appeared at low concentrations in some wells during the 2nd quarter, it was much higher during the 3rd quarter sampling with appearance of some vinyl chloride in a couple of wells. This pattern is consistent with active reducing conditions being slowly established. Since nitrate and sulfate had not been depleted the decline in TCE and appearance of ethene was unlikely to have occurred yet.

The soil samples in December all showed reduction of TCE from the baseline particularly in the highest zones of contamination. This is consistent with the increased solubility explanation given for the groundwater increase. *In situ* bioremediation of TCE has also been performed at Rocky Flats using HRC. Rocky Flats also experienced an initial lag and reduced rates of TCE reduction during the first 18 months (TIE, 2001, 2002). At the ACP site more sulfate is present then was initially recognized, requiring more HRC to deplete the sulfate that was present. Based upon these results and the planned 2 supplemental injections of HRC it was calculated that at the end of 3 years only a 25-50% reduction in mass could be expected.

The contractor proposed injecting a combination of lactate, HRC-X and HRC-primer at higher rates during year 2 and year 3. Lactate and HRC-primer are more soluble and would help reduce the electron acceptors faster. HRC-X has a slower release that would help maintain stronger reducing conditions for a longer period. They proposed injecting 35,400 lbs additionally vs. the additional 20,000 lbs originally planned. The change in composition and quantity of HRC resulted in increasing the proposed cost for the next 2 years from $261,497. to $422,674. These cost estimates were based on the cost of HRC injection only for the WMU.

Based upon the additional cost and uncertainty in meeting cleanup limits in 2005, RMIES elected to terminate the contract and the project. RMIES also received a cost estimate from Regenesis for remediation of the entire plume given the original estimates of TCE and TEA. Regenesis estimated that 18,798 lbs of HRC was required for an intial treatment of the plume at a cost of $103,389. This was only for the HRC. This suggests the additional area that the dilute plume represents will be much lower in cost to remediate then the source area, which is reasonable.

Unfortunately, the efficacy of the previous WMU *in situ* biostimulation using HRC is inconclusive at this point. Additional groundwater and soil sampling is necessary to see if the soil TCE has continued to decrease and that DCE, VC, and ethene have increased in the groundwater, concomitant with declines in sulfate, oxygen, and nitrate. Better techniques for oxygen and redox measurements also need to be tried, and more attention to TOC analysis as an indicator of electron donor availability. A few measurements for *Dehalicoccoides* using realtime PCR would also help to verify that the organisms that can completely reduce TCE are present and active.

If biostimulation is to be used on the source zone and the residual TCE, and as a method of bioimmobilizing on the U, the cost would likely exceed the estimate by the contractor, but not by more than 50% for the WMU estimate, alone. HRC-X would be a good long-term choice once reducing conditions for both TCE and U had been established, since it lasts for up to 3 years and would maintain reducing conditions with only an every other year or so injection. If only sodium lactate was used instead of HRC the cost would be $35K-105K for the lactate, but could require at least twice annual injections.

Regenesis has recently come out with a Metals Remediation Compound (MRC) which is a combination of polycystiene and polylactate. The mechanism of reaction is believed to be that metals will form a metal-organosulfur complex that will precipitate, the complex is slowly oxidized to release the metal, which is then bioreduced to a less soluble metal oxide. The HRC that is also in MRC would promote the reducing conditions for TCE simultaneously with the U reduction. Since the final U product is reduced, it is also subject to the same reoxidation concerns as using HRC or any electron donor. The MRC also has a strong smell due to the sulfur and biological deprotienation and putrification mechanisms could release hydrogen sulfide, which could make odor and handling an issue.

The advantage of MRC would be the immediate precipitation of the U and perhaps slower reoxidation to soluble U (Note: The mechanism is speculative and unproven at this point, but seems the best candidate). RMIES has also compared MRC, inorganic phosphates, organophosphates, chemical reductants, and HRC for their ability to remove soluble U in beaker studies and soil column. In these tests, the MRC brought 2 ppm U to <100 ppb in 10 days. With the exception of inorganic phosphates, which brought 1ppm U to <100ppb in 24 hours, the MRC performed better than any of the other compounds tested. However, since MRC is such a new product and has not been demonstrated completely it probably has to many uncertainties to meet the RMIES schedule.

A critical parameter needs to be determined to access the long-term feasibility of *in situ* bioremediation for U at this site. Are the high oxygen, nitrate, and sulfate concentrations observed in the CAMU typical for the whole site or are they only found there? Data from

1987 in other wells on the site suggest that the sulfate concentrations are normal for the site, but the nitrate is much higher than any other place on the site. The oxygen measurements are inconclusive. Since oxygen and redox is so difficult to measure accurately *in situ*, the site should continue measuring total organic carbon as an index of the amount of electron donor that might be available to sustain anaerobic conditions.

In general, if the ambient concentrations for these competing electron acceptors is much lower, then there is a much more reasonable expectation that once reducing conditions are established and the contaminants reduced, that they can be maintained without further addition of electron donors. The TOC concentrations measured in December 2002 at the WMU indicate that there is still insufficient electron donor to sustain reducing conditions. The site should also consider measurements for *Dehalicoccoides* once anaerobic conditions can be verified. Determining *Dehalicoccoides* using R-PCR will verify that the organism that can degrade TCE to ethene is present and active. The injection of liquid phosphate with the HRC would also be a better long-term strategy for the U reduction since the phosphate combines with U(VI) to form stable complexes under both oxidizing and reducing conditions. The U-phosphate would only release the soluble U if the pH fell below 5. Since these pH's are unlikely to be this low at Ashtabula this represents a better long term solution for the U. In addition, a single injection of phosphate would probably be all that is necessary.

The premise of this alternative is to provide a containment mechanism downgradient of the waste management unit to prohibit the possible migration of contaminants to the groundwater seepage face along the edge of the escarpment. This approach could be utilized alone or in combination with source and or plume treatment. The purpose is to reduce the potential/risk of elevated levels of groundwater contamination migrating through the upper brown silty clay and silt layer and seeping out along the face of the escarpment.

Hydrology

This option focuses on the upper 3-4 meters of glacial sediments characterized as an oxidized and fractured brown till that contains layers of silty clay and clayey silt that also contain silt lenses. It is estimated that this zone generally has a hydraulic conductivity of 10^{-5} cm/sec roughly two orders of magnitude greater than the underlying gray silty clay. Although there is some evidence that contamination extends into the gray clay, lateral migration of contaminants within this unit is not believed to be appreciable and containment is provided by the low permeability nature of the gray clay till.

Within and downgradient of the WMU, the topographic map of the upper surface gray silty clay (Figure 16) has a depression that trends roughly east to west. This depression generally coincides with a depression or swale in the surface topography, which slopes northward (Figure 17). This feature can also be seen on historic photographs of the area (Figure 18). These features are believed to influence and likely promote groundwater flow due to this locally thicker sequence of the upper brown silty till. Since this also represents a preferential pathway for contaminant migration this feature provides a good location for groundwater containment near the edge of the escarpment.
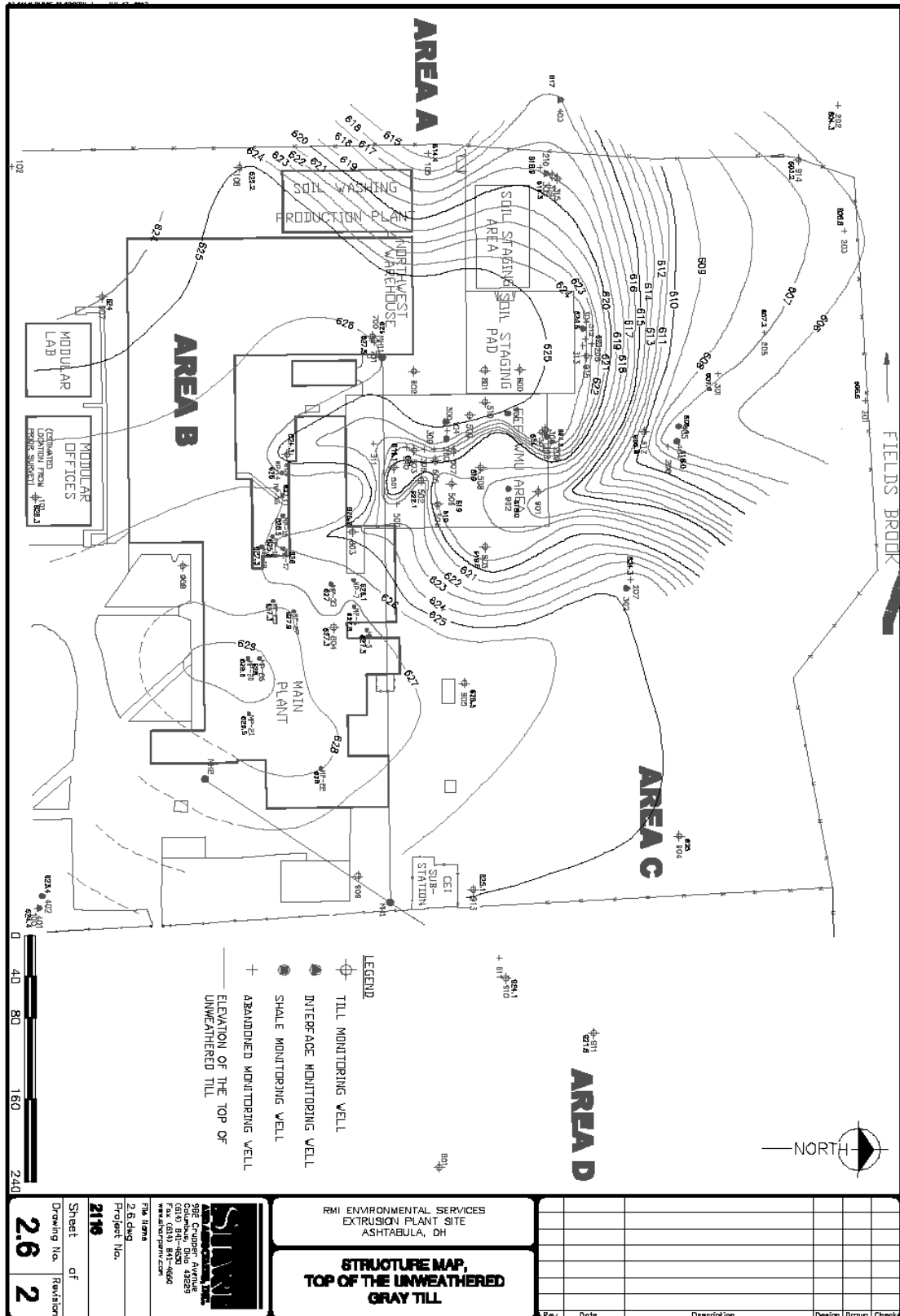
Figure 16. Structure map – Top of the unweathered gray till.
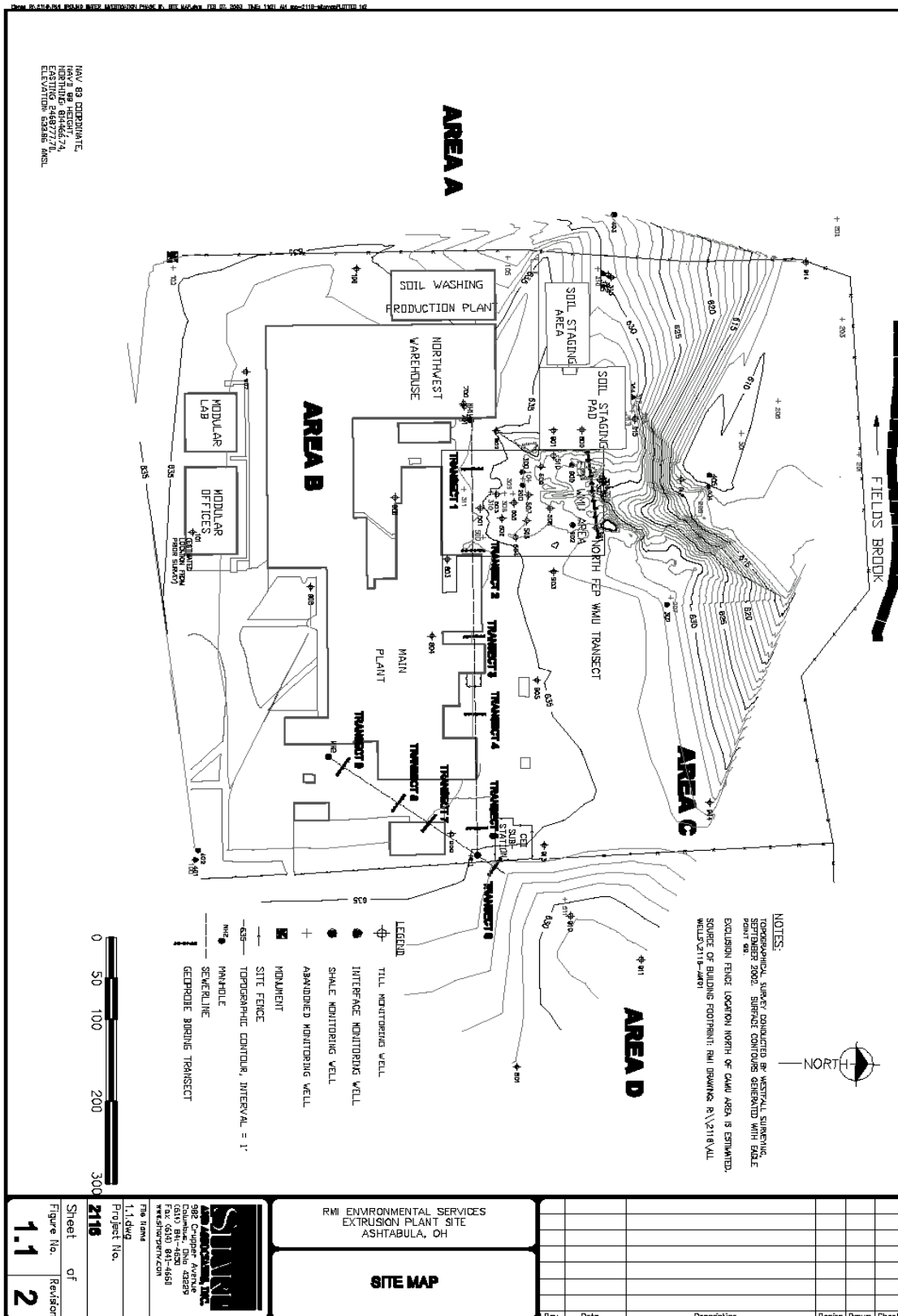
Figure 17. Surface topography at the ACP.
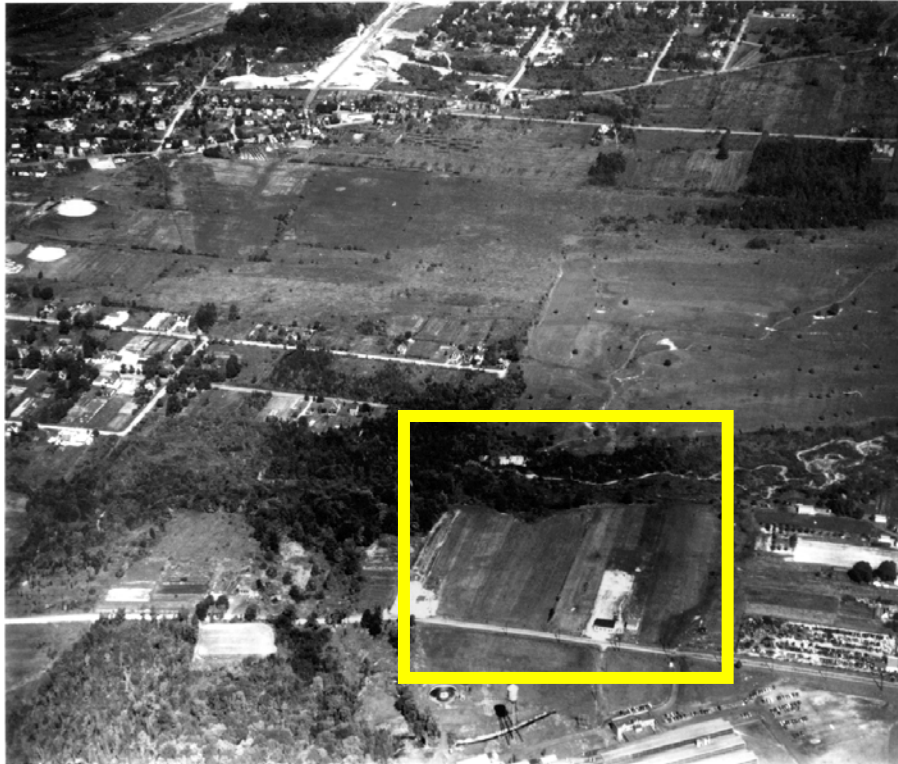
Figure 18. Historical photograph of north-sloping swale at the north end of ACP (photograph taken from the south looking north).

Three associated approaches related to containment of contaminated groundwater downgradient of the WMU include the following:

- **Downgradient Collection Trench with *Ex Situ* Treatment of Groundwater.** This approach would involve excavating existing soils down to and slightly into the gray silty clay along an east-west transect down gradient of the WMU (Figure 19). The trench would then be backfilled with a porous media, e.g., pea gravel, and designed so that water could be removed from one or both ends via active pumping or geodrain. The water would then be treated by an *ex situ* system and discharged to surface waters or possibly to sanitary sewers.
- **Downgradient Collection Trench with *In Situ* Treatment.** This option would involve excavation of soils possibly up to several feet down into the gray silty clay to provide a "sump" for placing amendment(s), which could reduce contaminant levels within the trench. The treated water would either then be actively withdrawn (pumped) or allowed to discharge by a passive means. If necessary, this could be combined with ex situ treatment if needed to meet discharge requirements. All of the configurations discussed earlier for use of a source excavations and possible amendments are also viable for a downgradient interceptor trench.
- **Permeable Reactive Barrier (PRB).** This technology utilizes a treatment material in a permeable trench or structure. The intercepted water is treated as it flows through the system and "clean" water is discharged. This technology has been the subject of active research throughout the world with investment by universities (Waterloo and

others), companies (e.g., Environmetal Technologies, Inc. and others), and all relevant federal agencies. The most common treatment material for VOCs is granular iron ("zero-valent iron"), amended granular iron, sorbents derived from industrial byproducts, or waste organic material for redox control. In the case of iron, the barrier provides an environment that dehalogenates chlorinated VOCs as they pass through because of the high energy of the surface corrosion reaction and the high surface area. The primary problems with iron based treatment technology relate to the chemistry of the water exiting the barrier, which often has a high pH (>10) and no dissolved oxygen. General problems include low treatment flow rate, especially in low permeability materials, sometimes expensive installation, and unknown lifetime of the barrier materials. For contingency measures, the design could include a sump and/or riser system so that groundwater could be withdrawn for ex situ treatment.
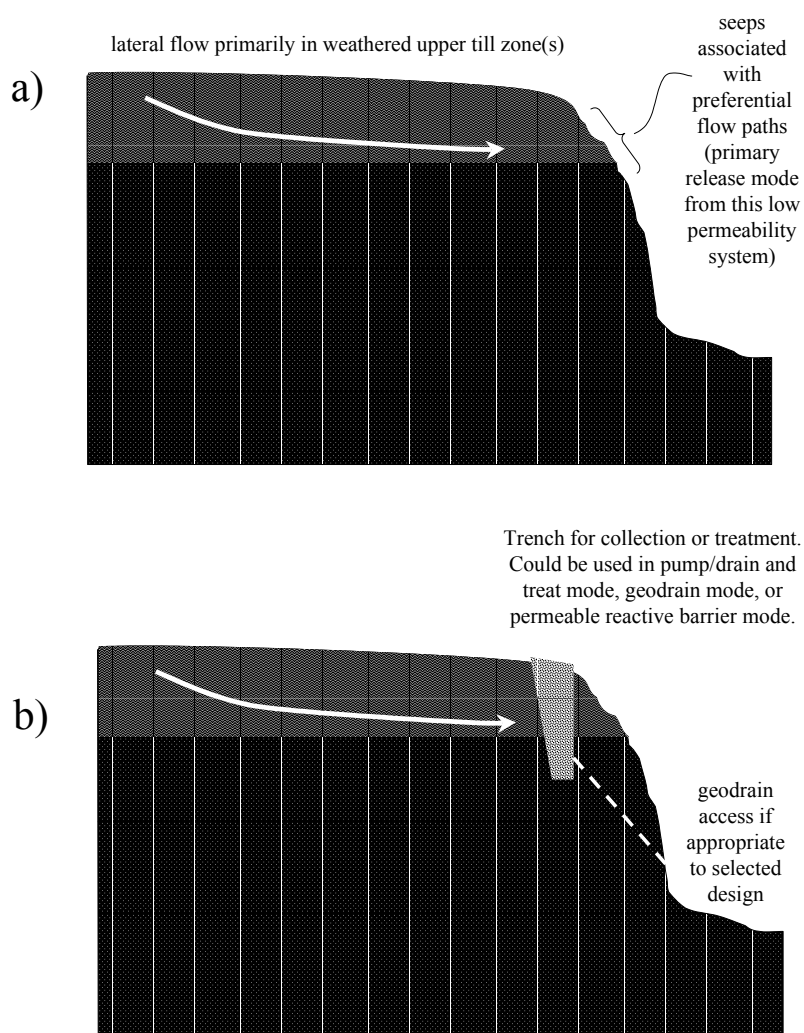
Figure 19. Simplified Conceptual Basis for Downgradient Collector / Interception System – a) baseline showing dominant lateral flow in weathered zones, b) proposed location of trench.

This technology represents a viable plume containment strategy for the ACP groundwater plume that is well matched to the site hydrology and geometry. Uncertainties with installation and lifetime increase technology risk for PRBs versus alternative downgradient collection/treatment systems. Specifics of appropriate use of permeable treatment materials includes collection trenches in the downgradient portion of the plume, eg. in the weathered till zone near the escarpment. Downgradient installation would provide plume release protection in this unique setting that has a low water yield and that does not justify active pumping and treatment. Downgradient collection and treatment systems may not be required if the plume is shown to be contained and not spreading and monitored natural attenuation is actively occurring. These systems will treat less contaminant than a central geosiphon/geodrain and will not provide as good an immediate control of the highest concentration plume after source treatment. However, all of the downgradient containment systems provide better containment at the plume boundary than the Geosiphon/Geodrain.

Potential Design Considerations

It appears that adequate information may exist to locate and construct a relatively simple groundwater collection trench. Two additional considerations regarding data collection and evaluation are also provided below. The intent of additional investigation is to increase the confidence in the placement and performance of a containment system. The ultimate determination of whether additional data is needed is up to the design team.

First, to properly design a collection trench with optional amendment(s) or a permeable reactive barrier (PRB), a very good understanding of the local groundwater flow regime is required. The upgradient area should be investigated to define hydrogeologic boundaries (depth to brown and gray clay, silt lenses, characteristics of backfill, and location of utilities). Areas adjacent to this investigation zone should be assessed for data gaps to ensure that local geologic and groundwater flow paths are well defined, especially where heterogeneities (silt lenses – especially in the upper oxidized sediments) may promote transverse migration to dominant groundwater flow paths. The full capture of the source zone and high-concentration-dissolved zones should be included in the designed extent of the trench/PRB, unless specific concentrations can be allowed to by pass the trench as part of a Monitor Natural Attenuation (MNA) program. The data collection phase would include obtaining the following discrete data (not fully inclusive):

- Water levels for key units including the weathered and fractured brown till, significant silt lenses, and lower gray till (layer-specific)
- Hydraulic conductivity data from brown till areas and available silt lenses
- Distribution coefficient data (for modeling considerations)
- Placement of performance monitoring wells
- Contamination data from wells to monitor trench/PRB performance.
- Installation of additional source area wells to ensure trench influence (gradient modifications) are propagating into the source zone to verify capture.

The data would be adequate enough to define:

- Local groundwater flow paths into and out of the source area and trench/PRB zone;
- Geologic boundaries to adequately estimate excavation volumes and construction costs (and specifications);
- Geotechnical conditions due to the near-by escarpment above the Fields Brook flood plain.

A second potential design consideration involves groundwater modeling. A numerical model of the WMU area would support remediation activities at the site. The model could be constructed to simulate groundwater flow in the clayey silt and silty clay components (including fill areas and silt lenses) of the upper weathered and fractured brown till. The transition zone to the more competent gray (unweathered) till could be used as a no-flow boundary in the model; thereby simplifying the calculation domain. The existence of silt lenses can be individually simulated where they exhibit a significant thickness in the weathered till zone, or where they are well correlated between boreholes. If layer simplification is required, the vertical integration of the silt lenses can be simulated in the model by having hydraulic conductivity higher where the lenses exhibit significant thickness.

The boundary conditions in the model will be assumed, except for the discharge along the escarpment, which could be simulated with drains or general head boundaries. The upgradient inflow to the model domain would have to be assigned by the user and subjected to an uncertainty analysis. The cross gradient boundaries would be either no-flow or general head boundaries to govern potential cross-gradient flow through the area. The model domain must be large enough to ensure that influence (draw down) from a collection trench would not propagated to an artificial boundary. The influences must be well contained in the central model domain.

Such a numerical model would be used to assess the performance of trench/PRB designs. The length of trenches, locations in the flow field, and configuration (straight, curved, chevron) could be evaluated to determine the zones of contribution (capture zones), influx rates under differing recharge conditions, and influences on the flow field that may affect source term treatments (flow velocities, treatment locations [i.e., HRC injection], and dewatering below a critical elevation).

An additional transport analysis could be performed to simulate plume degradation, radionuclide migration, and contaminant mass inflows to the trench. This can be used to estimate amendment volumes required to treat mass inflows.

Pump and Treat

Pump and treat is a standard technology that provides good performance for dissolved contaminants that can be efficiently collected. Pump and treat at the WMU (without concomitant source removal) is limited by the continued presence of a residual source and the high degree of heterogeneity. Thus, this technology would not be recommended without source removal unless the site was committed to long term operation (circa 100s of years). Slow desorption of solvents and U from the clayey material in the source area of the WMU and the low hydraulic conductivities (10^{-4} to 10^{-7} cm/sec), prevent this technology from being viable, except as an interim hydraulic containment strategy or a

technology for limited use in combination with other techniques. Pump and treat would be a long-term investment with an unpredictable endpoint and would require a different treatment for both the U and TCE. A particular limitation of pump and treat for ACP is the low flow rate that can be generated from each well – necessitating a large number of wells and complex operations. Note that the use of collection trenches at the downgradient edge of the plume is similar to pump and treat but has the advantage of being a more effective collection system, being able to use gravity to deliver water in some configurations, and providing an acceptable and intuitive containment strategy.

There are several enhanced removal technologies that are related to pump and treat – these technologies rely on injection of reagent to solublize or mobilize contaminants followed by effective collection of the high concentration water. There is a large body of literature related to uranium solution mining (based on sodium carbonate solution flushing). There is also significant literature and experience with the removal of residual undissolved TCE solvent using cosolvents and surfactants. Unfortunately, the low overall permeability at ACP and the probability of poor recovery reagents and tracers in this setting make these technologies undesirable. The potential for mobilizing contaminants without positive hydraulic control is a significant risk.

Monitored Natural Attenuation

MNA is defined as the stabilization and long-term shrinking of a contaminant plume (as defined by the isoconcentration contours).   In a technical sense, MNA is viable when the attenuation capacity of natural processes such as biodegradation or chemical reduction/stabilization are greater than or equal to the contaminant delivery (or loading). MNA is considered applicable to dissolved plumes only. This technology has been the subject of active research throughout the world with investment by universities, companies, and all federal agencies. The Department of Defense, Environmental Protection Agency, United States Geological Survey and DOE, in particular, have invested in the study of MNA for hydrocarbon contaminants. More recently, MNA protocols have been implemented for chlorinated solvents (EPA, 1998 and 1999). Protocols for metals or radionuclides are currently under development by several agencies (add references). The data suggest that MNA can play a role in a long-term strategy for responsible environmental management of challenging contaminants such as TCE, uranium and technetium at appropriate sites (i.e., sites with the potential for anaerobic dehalogenation and perhaps even stabilization of metals and radionuclides in naturally reducing environments or as stable minerals formed after phosphate amendments). Until the source term is removed at the WMU, it is unlikely that MNA would be acceptable to either the stakeholders or the regulators and therefore is not recommended as a short-term remedy for implementation prior to 2005. Importantly, the team consensus was that long term transition to MNA is critical to ACP and that MNA is ultimately the strategy that should be used on the dilute plume.

However, MNA will not be viable until: 1) documentation that the plume is stable or shrinking, 2) documentation of the attenuation capacity for the various contaminants, and 3) documentation that other source and plume treatment efforts have reduced contaminant loading to levels that are below the attenuation capacity. Depending on end use (free release or industrial/brownfield), risk assessment methods will be necessary to set technically based concentration limits for groundwater. It is likely that consideration of appropriate end states and other factors (the contaminated aquifers do not produce water at usable rates), that concentration limits can be safely raised to

levels above MCL. MNA will also require characterization, monitoring and initial verification, especially for U if it is to be used as a stand-alone technology after source removal. {add more specifics and references}.

MNA will be most acceptable to stakeholders and regulators as a follow up technology after an initial more aggressive treatment of the plume (eg. bioremediation). MNA is likely to be the optimal approach for this site only after following a phased through aggressive engineered source treatment, in combination with plume containment and treatment strategies.

Other Reagents (phosphates, peroxide, persulfate, permanganate, dithionate)

General Considerations

Liquid amendments can be, and often are, injected into the subsurface to treat groundwater contamination. In this case, there are two primary target objectives. TCE oxidation by strong oxidants or uranium precipitation by reduction or addition of phosphate. The reactions required to achieve these objectives are rapid and relatively complete. In addition, this technology is commercially available, relatively inexpensive, and could be deployed immediately. Injection can be done by installation of permanent injection wells or by temporary direct push technologies. Thus, this technology rates high for all of these categories, but suffers from one major obstacle. It is difficult to achieve wide-spread treatment in impermeable soils without a large number of injection points. This significantly increases costs and may render the technology inefficient relative to others.

The site has several biogeochemical parameters that will be drivers for the remediation of the WMU and long-term stewardship of the site. The low hydraulic conductivity will inhibit the efficient injection of stimulants, surfactants, oxidants, etc and the efficient extraction of the contaminants via either gas or liquid phases. TCE can be biodegraded via reductive dechlorination or oxidative co-metabolism. Oxidative co-metabolism is incompatible with reductive U stabilization because the less mobile reduced U would be reoxidized to the more mobile form. Reductive dechlorination of TCE can be incomplete if the correct organisms are not present, fortunately this is rarely the case. Complete reduction of TCE occurs optimally at reducing conditions where CO_2 can also be used as a terminal electron acceptor (TEA). U is reduced optimally when Fe(III) can act as a TEA. Thus, oxygen and nitrate must be depleted before U can be reduced and additionally iron and sulfate must be depleted before TCE can be reduced (see Figure 14). The WMU has high oxygen, nitrate, and sulfate. Depleting these TEA would require more electron donors (ED), i.e. carbon sources. This is doable but increases the cost. It appears that the rest of the site is high in sulfate but not in nitrate, oxygen in unknown. This creates some uncertainty in the ability of reducing conditions to stabilize U long-term. Stable phosphorus compounds complex with U without reduction and therefore are stable under both reducing and oxidizing conditions. The phosphate compounds; however, do not have any effect on the TCE. Liquid phosphates could be injected with the initial injection of HRC and would probably only need to be injected once, instead of multiple times.

Reductants and Phosphates

A number of carbon compounds have been demonstrated to provide biostimulation in the subsurface for the reduction of both TCE and U. These compounds could also be combined with air or oxygen injection for the co-metabolic degradation of TCE. Unfortunately oxidative mechanisms like this have no effect on U, indeed, they may even promote the reoxidation of U to the more soluble oxidized state. Some of the carbon sources that have been used for anaerobic dechlorination include: corn steep liquor, whey, flour, ethanol, molasses, vegetable oil, milk, sugar, methanol, cellulose, lactate, chitin, methyl cellulose, acetate, and polylactate (HRC). Lactate and HRC have been very widely used and are discussed more thoroughly in the section on *in situ* bioremediation. The lactate, chitin, methyl cellulose, and HRC are the most expensive ranging from $1-12/lb, respectively. All of the others range from $0.02 to 0.80/lb. The later group, are all byproducts that are normally wasted in mass. Many of them have issues since they can contain a mixture of compounds, some of which may not degrade completely and some of which may be flammable or have special handling considerations. To date only molasses, vegetable oil, lactate, acetate, and HRC have been demonstrated to effectively reduce U; however, the same basic reductive mechanism should work for all of these carbon amendments since the principle of providing an electron donor to the indigenous bacteria would stimulate them to grow and deplete TEA in the following sequence: oxygen, nitrate, Fe(III), sulfate, and carbon dioxide. TCE cannot be respired until CO_2 redox conditions are reached; however, U can be reduced once Fe(III) starts to be reduced.

Stabilization of uranium can be achieved by either reducing it to the U(IV) valence state or by forcing precipitation of insoluble phosphate phases. Reduction is less attractive than precipitation as a phosphate because the reduced phase may be subject to re-oxidation and dissolution. However, reduced uranium phases may be longer lived in systems in which all electron acceptors (e.g. NO_3-, O_2, and SO_4-2) are depleted. Uranium phosphate phases can be quite stable for long periods of time as evidenced by the presence of natural analogues in geologic systems. Dithionite is a partially reduced sulfur compound that has been used as a reductant for metals including Cr(VI), Tc-99, and U (add references).

Stabilization by a phosphate addition can use a variety of injectable chemicals. These include inorganic phosphate salts such as trisodium phosphate and organic phosphate compounds such as triethyl phosphate (TEP) or tributylphosphate (TBP). The inorganic salts promote direct precipitation of uranium phosphate phases by elevating dissolved phosphate until saturation indices of uranium phosphate phases are exceeded. The organic solutions require microbial degradation prior to their release of phosphate. This adds some uncertainty because of the reliance on microbial processes. Studies at ACP suggest that TEP and TBP were less effective than dissolved inorganic salts.

Oxidants

Chemical oxidation uses reagents to destroy high concentrations of contaminants (typically non-aqueous phase liquids). Because *in situ* oxidation requires delivery of reagent and requires intimate contact of the reagent with the source solvents, it would work well in an excavated soil system where the geometry and flow characteristics could be carefully controlled. However, it would not work well *in situ* at ACP because of the

limited permeability of the sediment. A factor that would improve performance is the presence of more permeable stringers – these probably have a significant role in plume migration at the waste management unit at ACP and the reagents would follow the same pathways – nonetheless, efficient implementation of a liquid based reagent treatment at a site where optimistic injection rates for a well are in the range of < 1 gpm is unlikely.   If viable, such a treatment would be able to meet schedule requirements (assuming that a system could be set up and operations started in a timely fashion) because it is an aggressive and rapid method. Typical treatment reagents include Fenton's reagent (hydrogen peroxide and reduced iron), persulfate, or permanganate solutions. These reagents are strong oxidizers that "burn" the contaminant in a saturated or moist soil setting. As the reagent is added, it reacts vigorously and often induces bubbling and mixing – a process that may enhance contact of the reagent with the target contaminant or in a low permability system may clog the formation with a separate gas phase. Several variants of *in situ* oxidation methods have been deployed commercially. A key element to the success is performing the work rapidly with a minimal volume of reagent. Specific attributes that make this technology promising includes: relatively small and well-defined highly contaminated and permeable target soils. The technology uses large volumes of reactive reagents, is moderately difficult to deploy (i.e., requires expensive infrastructure), requires good access the groundwater system, requires low ambient pH for Fenton's reagent, and many similar challenges. This technology will also reoxidize reduced forms of uranium, U(IV), chromium (III), and other metals, which are relatively insoluble. Reoxidation not only transforms these metals and actinides into the more soluble forms U(VI) and Cr(VI), but also makes them more toxic in the case of Cr. This increased mobility could also become an issue during and ex situ treatment process, in terms of disposal of the leachate. Since safer, less-expensive, and effective alternative technologies are available, chemical oxidation is not recommended.

Thermal Treatment

Several types of thermal enhancements are available with different characteristics and applicability to different conditions. These technologies include self resistive ("Joule") heating, steam, and radio frequency heating. Because of the low permeability sediments in the WMU Area, the following discussion focuses on self resistive ("Joule") heating. This technology directly "injects" AC power into the subsurface through resistance to the flow of electricity in the bulk soil/groundwater; heat is generated. Thus, the ground itself acts in a manner analogous to the heating element in a small radiant home or office heater.

This process normally requires some moisture to be maintained in the heated zone. Since the area immediately adjacent to the electrodes heats faster than the overall treatment zone, injection of small amounts of water or electrolyte solution is often required to allow the ground to be heated to temperatures near 100° C and the collection of contaminated vapor. A relatively successful commercial variant is called six-phase heating. Dividing the power into six phases (rather than the traditional three phases of line power) helps avoid problems because the power density near each electrode is reduced and the overall power pattern is more uniform. An advantage of six-phase heating for vadose zone contamination is that power and heat are preferentially directed into fine grained or clayey layers. Six phase heating was developed by the Pacific Northwest National Laboratory and has been licensed for commercial implementation. Six-phase heating is potentially applicable to similar solvent source targets as steam but with less robustness to heat below the water table and the possible need for closer

borehole spacing to install electrodes. Six-phase heating is likely to be more robust than steam for low permeability conditions. Heating is an aggressive and viable technology for addressing the highest concentration TCE source zones.

The geological conditions in the source area of the WMU are suited to Joule heating so it remains a viable method. Collection of the contaminant vapors from the heated zone remains a challenge. This technology would have no effect on the U and Tc-99. As a result, this approach has some technical risk. Heating is unlikely to be useful for large areas (as a general source or plume cleanup tool) in the WMU area but may have applicability for TCE sources where the radionuclides meet their relevant soil cleanup standards. Selection of this technology should be made only as part of a comprehensive strategy if aggressive TCE removal is justified. Several commercial vendors are available for this technology (at least two U.S. companies and a Canadian company) and there is an increasing application base. Of particular note is the use of this technology at Paducah and proposed uses in Ohio.

Air Sparging

This technique, based on injection of air below the water table, has limited applicability to TCE plumes in low permeability soils, to layered or heterogeneous systems and to dense residual solvent pools located deep within an aquifer. Air sparging has no potential benefit for uranium or technetium. Air sparging is most applicable to permeable and homogeneous sites where volatile contaminants or contaminants that would benefit from addition of oxygen are located in the upper portion of the system (allowing the air to be injected below and then move upward due to buoyancy). Because sparging requires well-understood and controlled delivery and spread of air and intimate contact of the air with the source solvents, it would have almost no applicability to the source area for the ACP WMU plume, which is in heterogeneous and low permeability sediments.

Electrochemical Treatment

Electrochemical Treatment is a recently proposed and implemented technology that uses electrical current as the central component of a system to decontaminate contaminated soil in place. Similar to the more aggressive direct energy thermal techniques (e.g., six phase heating and radiofrequency heating), these treatments rely on injecting electromagnetic energy directly into the bulk soil. Thus, the considerations of geology, water content, etc are similar with these methods as with the related thermal methods. The key difference in these "treatment" methods is the additional implementation and documentation of a destruction or detoxification mechanism in the deployment process. Two variants, at different levels of maturation are discussed below. These are the Lasagna technology and the ElectroChemical Remediation Technology (ECRT).

The most documented electrochemical treatment to date is the Lasagna system developed and implemented by a consortium from federal researchers (DOE, EPA and others) industry and universities. Lasagna is primarily an electroosmosis process that relies on moving water through the subsurface. This technology exploits phenomena in which ions in the diffuse double layer near soil particles move in response to a DC electric field and induce water movement in a parallel direction via shear forces or drag at the double layer interface. The unique feature of Lasagna is placing layers of treatment or capture material in the path of the moving water so that the contaminants

are efficiently detoxified as they move over relatively short distances. The system also minimizes the problems sometimes associated with the chemistry near the electrodes by treating the contaminants relatively far away within the target treatment volume. While the basics of this technology are well established from industrial applications in dewatering and clay consolidation, fully reliable performance for remediation applications has yet to be established. The technology is most applicable to near saturated sediments with low permeability (e.g., < 10-5 m/s hydraulic conductivity). Within this bound, the method has low power consumption and will induce a relatively uniform flow that is "independent" of heterogeneity. For organics, the method is limited to the soluble fraction and will not remove residual nonaqueous phase solvents in the system nor will it treat tightly bound contaminants.

ECRT is a recent technology that has been investigated in Europe (P2-Soil Remediation, Inc) and in the United States (by Weiss and Associates in partnership with the developers). The technology advocates suggest that soil can be decontaminated using much lower current densities than Lasagna or heating methods. In particular, they indicate that organics such as TCE can be effectively treated in place by "induced oxidation" processes that they designate Electrochemical GeoOxidation (ECGO). The claims are supported by patents (US 5,738,778 and 5,596,644) and by limited field data. Importantly, the developers do not have controlled documentation about the destruction process and do not know mechanism of destruction nor its robustness. They speculate that "these reactions occur at any and all interfaces within the soil" and that "an induced polarization field is produced …{leading to} … disharges of electricity to occur … {and that} … in the electrical discharge, REDOX reactions take place." It is unlikely that "discharges" are occurring at the power densities employed and significant additional research is needed before this method can be reliably used. As with most other direct energy processes, the data suggest that reaction rate is inversely proportional to grain size and that moisture in needed in the system. Based on the case studies, the proposed technology is intriguing and, if substantiated by additional research, may be important in the future. Despite their isolation and available environmental, the conditions in the WMU do not appear ideal for ECRT/ECGO. The geochemical conditions appear substantially different from those of the anecdotal studies reported to date. Most importantly, however, the technology is sufficiently immature that the project could not be performed in any mode except a research mode – significantly increasing costs for monitoring and incurring potential schedule risk. Based on the available information, this technique would be viable if it performed as claimed by its vendor. These claims appear optimistic and deployments should be selected carefully to minimize potential downside risks if the technology fails while at the same time encouraging disciplined technology development for this type of inexpensive and potentially revolutionary method. According to Weiss and Associates, the active redox zone reacts and destroys organics while metals migrate to both electrodes for easy collection and removal. Treatment is reportedly cost effective, but does take months and requires wetting of the soil volume being treated. Despite the reported track record in Europe, the team did not recommend this technology because of its immaturity and its limited track record. Even if the technology works, understanding of the basic mechanisms is limited despite the explanations in the vendor literature.

RECOMMENDATIONS

A technology matrix was prepared to identify and compare viable technologies. In the technology matrix, the key aspects and issues for each technology are provided relative to site specific goals and the baseline remedial strategy. The current remedial baseline strategy combines excavation of the source followed by installation of passive treatment with amendments. A description of criteria used to compare the technologies or approaches is listed below.

The first column describes the technical objective for using the technology, specifically, whether it is appropriate for treatment of the source area, treatment of the dissolved plume, or for containment of the plume. This column also notes whether the system is predominately active or passive. In the subsequent columns, the technologies are evaluated relative to the current baseline of excavation for the following criteria: Effectiveness, Regulatory and Public Acceptability, Implementability, Schedule, Cost, Long Term Performance, and Technical Maturity. Each of these criteria is described below:

- The **Effectiveness** column describes how site specific technical conditions such as permeability or lithology may impact remedial performance.
- **Regulatory and Public Acceptability** considers how the technology will be accepted by regulatory and stakeholder groups. A ranking of high indicates the technology should be favored over the baseline.
- **Implementability** identifies considerations associated with site logistics, health and safety issues, footprint needs, etc.
- The key parameter for **Schedule** is whether the technology can be implemented by the 2005 closure deadline. The expected duration of system operation is also noted.
- **Cost** estimates the cost of implementation of the technology, specifically, high cost systems exceed five million dollars, medium range from to 2 to 5 million, and low cost systems are less than 2 million.
- Key issues addressed under **Long Term Performance** of the system include whether the system eliminates long term liability and an estimation of whether the technology is likely to be effective over an extended period of time. A high ranking indicates the performance of the system should be higher than the baseline system.
- A ranking of high under **Technical Maturity** of the program indicates that the system is widely available in the commercial market place.
- In the last column, the technology is given an **Overall** ranking as either a viable or not viable for this site application.

Two technology matricies were prepared. The first matrix includes technical approaches that use excavation as the first remedial step. These approaches are appropriate to address current final clean up levels of 30 pCi/g. The second technology matrix evaluates technical approaches designed to meet the higher U clean up goals of 100-125 pCi/g that may be appropriate if a risk-based clean-up level is developed and accepted at a later date. These matrices are provided on the following pages.

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Technology Matrix 1: Excavation-Based Groundwater Remediation

Remediation Technology	Objectives	Effectiveness	Regulatory and Public Acceptability	Implement-Ability	Schedule	Cost	Long term Performance	Technical Maturity	Overall
Excavation followed by geodrain with amendments	Source treatment and plume containment and treatment Passive after period of contingency ex situ treatment	Reduces hydrologic driving force for plume expansion. Relatively effective for capture in upper weathered portion of system where plume migration primarily occurring – especially for capture of water from more permeable stringers. Amendment effectiveness uncertain. If not effective, ex situ treatment may be needed (or closure of geodrain). Can be operated in continuous flow mode or in a batch mode depending on design criteria.	Medium to high – general concept acceptable but final acceptability based on including system in an overall acceptable strategy and in identifying promising blend of amendments and implementing contingency treatment	Implementable with standard construction techniques following excavation	Can be implemented by 2005 if decision finalized System would require operation and monitoring until plume concentrations meet environmental protection standards If amendment proves effective, or if passive ex situ treatment proves viable (e.g., wetland treatment) then active ex situ treatment can be discontinued.	Implementa-tion costs Medium $2-5M O&M relatively low cost for 0.5 gpm nominal flow rate until passive systems are proven Lifecycle costs Medium	High Approach eliminates long term liability associated with source and is likely to be effective over an extended period. Implementation includes robustness to minimize risks of portions of the concept not working (e.g., if amendments do not work).	Unique concept – past developments for PRBs and other similar technologies are relevant	Viable. Current baseline. Reasonable choice if amendment blend selected carefully and if large scale excavation planned. Represents good linkage and beneficial use of infrastructure from related activities.
Excavation followed by geodrain with ex situ treatment (no amendments)	Source treatment and plume containment and treatment Active if system uses traditional treatment, passive after period of contingency if wetland or other passive ex situ	Reduces hydrologic driving force for plume expansion. Relatively effective for capture in upper weathered portion of system where plume migration primarily occurring – especially for capture of water from more permeable stringers. Can be operated in continuous flow mode depending on	Medium to high – general concept acceptable but final acceptability based on including system in an overall acceptable strategy	Implementable with standard construction techniques following excavation	Can be implemented by 2005 if decision finalized System would require operation and monitoring until plume concentrations meet environmental protection standards If passive ex situ treatment proves viable (e.g., wetland	Implementa-tion costs Medium $2-5M O&M relatively low cost for 0.5 gpm nominal flow rate until passive systems are proven	High Approach eliminates long term liability associated with source and is likely to be effective over an extended period.	Unique concept – past developments for collection trenches and other similar technologies are relevant	Viable. Reasonable choice if large scale excavation planned. Higher risk of requiring long term active treatment of collected water than system with amendments.

Technology Matrix 1: Excavation-Based Groundwater Remediation

Remediation Technology	Objectives	Effectiveness	Regulatory and Public Acceptability	Implement-Ability	Schedule	Cost	Long term Performance	Technical Maturity	Overall
	treatment implemented.	design criteria.			treatment) then active ex situ treatment can be discontinued.	Lifecycle costs Medium			Represents good linkage and beneficial use of infrastructure from related activities.
Excavation followed by backfill and no geodrain	Source treatment and limited plume containment	Results in low permeability zone within original source excavation and will plug the permeable pathways adjacent to the original source. Combined with regarding, the water driving forces will be reduced.	Medium Neutral strategy that would likely need to be combined with alternative plume treatment and containment strategies	Implementable with standard construction techniques following excavation	Can be implemented by 2005 if decision finalized No continued operation requirements	Implementation costs Low <$2M O&M not required Lifecycle costs Low	High Approach eliminates long term liability associated with source and is unlikely to be effective for plume treatment	mature	Viable. Reasonable choice if alternative plume treatment or containment used. Does not strongly leverage access and infrastructure resulting from excavation.

Technology Matrix 2: "Other" Groundwater Plume Remedial Options

Remediation Technology	Objectives	Effectiveness	Regulatory and Public Acceptability	Implement-Ability	Schedule	Cost	Long term Performance	Technical Maturity	Overall
In Situ Bioremediation	Source and plume treatment using anaerobic biological degradation and stabilizing TCE Active approach	Medium given ability to address VOCs and U – low given permeability issues and difficulty injecting.	High – already permitted.	High given that it has already been implemented at ACP.	Likely to be implemented by 2005, but may need to operate longer because of issues with DO and electron receptors.	Low for implementation. If lactate is used, costs are reduced. Life cycle costs may be higher if there is a continuing need for electron donors.	Medium given need for periodic electron donors, but could be high if phosphate is added (in addition to lactate).	High. Lower for U if reoxidizing conditions exist.	Viable – recommended for source if no excavation.
Downgradient Collection Trench with *Ex Situ* Treatment	Containment with passive collection and active treatment	High from a containment perspective.	Medium to high given that it leaves source in place.	Medium to high – logistics, slope stability, hydrogeologic considerations are complicating factors. Health & safety issues may be of concern.	Likely implemented by 2005. Duration depends on design criteria (i.e., when to shut off).	Implementation costs are low to medium; O&M costs are low; life cycle costs are low to medium, taking into account *ex situ* treatment.	High over extended period, but medium to low in terms of eliminating liability (source remains).	High – trench emplacement is well proven.	Viable – especially if site-specific source remediation goals are considered.
Downgradient Collection Trench with *Ex Situ* Treatment (with contingency treatment period)	Passive collection and passive treatment with potential for active treatment	High from a containment perspective.	Medium to high given that it leaves source in place.	Medium – logistics, slope stability, hydrogeologic considerations are complicating factors. Amendment design and selection are also issues. Health & safety issues may be of concern.	Likely implemented by 2005. Duration depends on design criteria (i.e., when to shut off).	Implementation costs are low to medium; O&M costs are low; life cycle costs are low to medium, taking into account *ex situ* treatment.	High over extended period, but medium to low in terms of eliminating liability (source remains).	Medium – some risk with amendment selection, although trench emplacement is well proven.	Viable – especially if site-specific source remediation goals are considered.
Permeable Reactive Barrier	Containment with passive collection	Medium to high, depending on	Medium given that it leaves	Medium – based on selection of	Implementation by 2005	Implementation costs are low to	Medium – does not eliminate	Medium	Viable – especially if

Technology Matrix 2: "Other" Groundwater Plume Remedial Options

Remediation Technology	Objectives	Effectiveness	Regulatory and Public Acceptability	Implement-Ability	Schedule	Cost	Long term Performance	Technical Maturity	Overall
	and passive treatment	amendment selection and barrier placement.	source in place.	amendment. Logistics, slope stability, hydrogeologic considerations are complicating factors. Health & safety issues may be of concern.	may be a challenge based on amendment mix and design criteria. Hydrology needs to be very well understood.	medium; O&M and life cycle are low.	source liability. Amendments may not be sufficient for the life of the plume.		site-specific source remediation goals are considered. There is some risk associated with the need for lifetime emplacement – may require more monitoring than other options.
Pump and Treat	Plume containment	Poor in low permeability soils when using wells.	Medium – does not address source contamination.	High – except for operating collection system in low permeability soils. Also large number of wells required.	Can be implemented by 2005.	Implementation costs are low, O&M costs are low, life cycle costs are low to medium given duration of operation.	Medium – given source is left behind.	High/mature	Viable but there are better options.
Monitored Natural Attenuation	Passive plume treatment	Limited for plumes that contain high concentrations, given limited capacity for contaminant degradation/stabilization.	Low in the short-term, high in combination with source treatment technologies.	Requires modeling and validation – protocols are in place for TCE and are being developed for rads.	Cannot be implemented by 2005 in light of site-specific goals.	Implementation, O&M, and life-cycle costs are low.	Low – must be used in combination with other technologies.	Medium	Viable – and highly recommended as long-term strategy but must be used in combination with other technologies (along with long-term monitoring).

Technology Matrix 2: "Other" Groundwater Plume Remedial Options

Remediation Technology	Objectives	Effectiveness	Regulatory and Public Acceptability	Implement-Ability	Schedule	Cost	Long term Performance	Technical Maturity	Overall
Other Reagents (phosphate, peroxide, persulfate, permanganate, dithionate)	Plume remediation/destruction of TCE and stabilization of U	Medium – reactions are rapid but medium is difficult to inject into low permeability soils. Some reagents may release gases, which is problematic.	High – numerous reagents deployed at many sites.	Medium – logistics are simple but injecting reagents is difficult. Health and safety issues exist given reactivity. Oxidants and reductants are not typically viewed as ideal for injection into low permeability soils.	Can be implemented by 2005. Some schedule delays associated with injection are possible.	Implementation, O&M, and life-cycle costs are medium.	Depends on whether you target TCE or U. Temporary or permanent for U and permanent for TCE.	Mature	Potential viable – might be used for source treatment rather than general plume treatment. Phosphate may be used in combination with *in situ* bioremediation.
Thermal Treatment	Source treatment for TCE (no treatment for U and Tc99)	Effective for removal of TCE in low permeability soils assuming that system is dried.	Medium – has been used and accepted	Medium for limited source zone area	Implementation by 2005 possible.	Implementation costs are medium; O&M costs are low (short term operation); life cycle costs are medium.	Good for TCE source but not for U.	Medium to high given limited deployments.	Viable for the TCE source - selection should be based on overall strategy of the site.
Air Sparging	Source treatment	Ineffective for heterogeneous low permeability media. Targets solvents but does not address uranium.	Low -- ineffective	Low	NA	NA	NA	NA	NA
Electrochemical Application	Source treatment	Some applications such as LASAGNA may be feasible but challenging to implement at this site	Medium – has been tested at Oak Ridge (some variants speculative and not acceptable)	Medium	Implementation by 2005 challenging	Implementation Medium to High O&M Medium	Depends on design and performance. Insufficient data to predict	Low to Medium	Potentially viable, but there are better alternatives

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APPENDIX A – Acronyms and Abbreviations

ACP	Ashtabula Closure Project
ALARA	As low as reasonable achievable
CAMU	Corrective action management unit
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act
DOE	U.S. Department of Energy
DOE-OH	DOE Ohio
DP	Decommissioning plan
ECRT	ElectroChemical Remediation Technology
EM	DOE Office of Environmental Management
EM-50	DOE Office of Science and Technology
K_d	RESRAD partitioning coefficient
LLW	Low-level radioactive waste
MCL	Maximum contamination levels
MDA	Minimum detectable activity
NRC	U.S. Nuclear Regulatory Commission
OEPA	Ohio Environmental Protection Agency
OH	DOE Ohio Field Office
ODH	Ohio Department of Health
PRG	Preliminary remediation guideline
RESRAD	Residual radioactivity [computer code]
RCRA	Resource Conservation and Recovery Act
RMIES	RMI Environmental Services
SAIC	Scientific Applications International Corporation
TCE	Trichloroethylene
TEDE	Total effective dose equivalent
USACE	U.S. Army Corps of Engineers
USEPA	U.S. Environmental Protection Agency
VOC	Volatile organic compound
WMU	Waste management unit

Units

cm^3	Cubic centimeters
g	Gram
hr	Hour
L	Liter
m	Meter
mCi	Millicurie
millirem	0.001 Roentgen equivalent man
µCi	0.000001 curie
pCi	10^{-12} curie
yr	Year

APPENDIX B - Technical Assistance Request

TECHNICAL ASSISTANCE REQUEST
ASHTABULA CLOSURE PROJECT
ACP 03-03-3

Field Deployment of Direct Push Technology For TCE Plume Delineation and Evaluation of Off-site Mitigation Controls

Section 1 -- Approvals for Technical Assistance: {original signed were indicated}

_____   _____
Contractor Site Representative   OST/HQ Program Manager

_____   _____
DOE Site Manager   OST/HQ Office Director

_____
DOE OH Manager

Section 2 -- Background and Problem Description:

The groundwater at the ACP site is contaminated to above drinking water standards and the soil above cleanup levels with trichloroethylene (TCE), uranium (U) and technetium (Tc). The current baseline for the soil in the Former Evaporation Pond (FEP) Waste Management Unit (WMU), previously referred to as the Corrective Action Management Unit (CAMU), is *in situ* bioremediation to remove the TCE followed by excavation and shipment off-site to Envirocare as low level waste (LLW). Although the bioremediation is expected to reduce TCE in soil, two uncertainties exist: 1) Whether the kinetics of *in situ* treatment will fall within the time constraints for site closure; and 2) Whether TCE in the groundwater will fall below maximum concentration levels (MCLs) for drinking water. The cleanup criteria for water, established to allow termination of the NRC license is 5 ug L^{-1} for TCE, 30 pCi L^{-1} for U and 90 pCi L^{-1} for Tc.

As a result of these uncertainties, a TA request was issued by the site that sought evaluation, recommendations, development, and application of a process to treat source material of approximately 6,600 cubic yards of soil/sediment contaminated with organic solvents (TCE), Tc-99, and U in the FEP and associated groundwater plume. A TA Team was assembled at the ACP in late June to address uncertainties associated with remediation of the FEP area and groundwater. As a result of this TA meeting a final report was issued, "*Recommendations to Address Contaminated soils, Concrete, and Corrective Action management Unit/Groundwater Contamination at Ashtabula, Ohio*" that addressed these areas and made recommendations for follow-on activities.

Section 3 -- Scope:
The scope of this TA for the ACP is derived from recommendations contained in the TA report. The recommendations for groundwater and the FEP were combined since characterization and remediation could not realistically be separated in this area.

1. First, the team recommended that direct-push technology be used to further characterize the site including the FEP source area and plume to support the design and optimization of the remedial system. There is a need to simultaneously better define lithology, determine which wells can be abandoned and where new wells may be needed, enhance the conceptual site model, and design a monitoring strategy using multiple, real-time measurements (e.g. SCAPS Cone Penetrometer, beginning late fiscal year 2002).

2. Second, the team recommended that the site accelerate excavation (excavate FEP and 18 inch line in FY-03), thereby eliminating two years of HRC injection that would otherwise be coupled with expensive monitoring and research studies. Excavation would remove technetium-99 (Tc-99) and most of the TCE and U source terms. The excavated material could be treated quickly with soil vapor extraction to treat the TCE, which is classified as 'characteristic' and shipped to off-site disposal as LLRW at Nevada Test Site (NTS).

3. Third, a down gradient drain (Geodrain) or a siphon (Geosiphon) pipe from the bottom of the source excavation to the bottom of the nearby escarpment is also recommended after the source material is removed. This gravity induced pumping of the surrounding aquifer should pull most of the residual contaminated groundwater to one location for treatment or discharge. The drain water could be treated using the existing wastewater treatment facility, if necessary. When the drain or siphon is installed, the previous characterization data could be used to decide if additional lateral horizontal wells from the excavated area might improve control of the residual contaminant plume. The excavation area could also be backfilled with high permeability material and amendments (e.g. reductants & phosphate). Other options, such as passing drain water through an amendment containing system at the drain outlet prior to release are feasible.

4. The next step, which could be scheduled to take place at the end of fiscal year 2004, would be to monitor the Geodrain for one year in order to establish trends in groundwater contaminants of concern. If monitoring data indicates a need, the site should consider amendments to reduce residual on-site groundwater contamination levels to allow license termination (e.g. reductants, HRC). If additional amendments are deemed necessary, the site should investigate research and development activities that will provide the best alternatives (such as NABIR, EMSP, SERDP, ESTCP, and others). As part of the long-term strategy, the site could transition the groundwater plume to MNA.

5. Finally, the site should also consider a risk-based assessment, especially for the residual uranium contamination. The current approach of biostabilization

or any *in situ* stabilization approach will have to depend on reduction or adsorption *in situ*. The stabilized (reduced and adsorbed) U is likely to reoxidize and become more mobile at least transiently throughout the plume on long-term basis. Given the lack of risk receptors and the intended permanent industrial use for the site this risk-based assessment of the plume might greatly reduce remediation and monitoring needs and allow the site to terminate the ODH radiation license.

Section 4 -- Scheduling Requirements:
Consistent with the present site remediation schedule, DOE-ACP has identified this TA as a top priority and is requesting immediate TA support. The estimate duration for this TA is ca. 12-18 months. The major element in this TA request is the need for technical experts to provide sustained support to assure that any appropriate recommendations can be successfully implemented. This support will focus on the following areas in a sequential but integrated basis beginning as soon as possible:

1. Assistance with Characterization activities for the CAMU (CPT, MIP, etc.)
2. Assistance with design for excavation and *ex situ* treatment of soil prior to off-site disposal
3. Assistance with design and optimization of Geodrain or Geosiphon
4. Evaluate monitoring data for amendment need or selection
5. Assist in risk assessment
6. Provide links to R&D for amendment selection, design review, readiness reviews, and provide source documentation for precedence, functional design criteria, etc.

Section 5 -- Benefits:
The primary potential benefits of this TA will be:

1. Reduction in uncertainty to achieve the 2006 closure date by immediately addressing regulatory issues associated with groundwater cleanup and site closure, potentially reducing schedule and therefore cost
2. Reduction in disposal cost for the estimated 6,600 cubic yards (cy) of excavated WMU soils as LLW ($135/cy) vs. MLLW ($540/cy) could be in excess of $1 million as a result of *ex situ* soil treatment to remove TCE.

The cost estimate to fund this TA for a 12-18 month window support is about $75K, and it is anticipated that a cost saving of over $1 million or more should result from TA recommendations in the areas listed above.

Section 6 -- Deliverables:
Deliverables will include support documentation for the areas identified in Section 4 to support characterization, excavation, and remediation of the FEP. This information will be presented to DOE and Contractor management in a progressive manner has tasks are initiated. It is anticipated that during completion of various stages of the project that status reports are prepared and issued to DOE and contractor management.

APPENDIX D - Approximation of Flow and Radius of Influence

**Spreadsheets Documenting Calculations
and graphs in metric and traditional engineering units**

estimated flow from excavation and radius of influence

assumed	high	3.00E-05 cm/sec	(approx)	somewhat higher than range measured in slug tests to account for heterogeneity and other factors
hydraulic conductivity	median	5.00E-06 cm/sec	(approx)	
	low	1.00E-06 cm/sec	(approx)	

other assumptions

Reference:
Powers, J. P., 1981.

rs = 15 m — Construction Dewatering: A Guide to Theory and Practice.
H = 8 m — John Wiley and Sons, New York, 484 pp.
h = 5 m — (all equations numbers and page numbers on this sheet are for this reference)
drawdown = 3 m
b = 10 m
Cs = 0.2   section 4.3

estimate Ro from Jacob

				equation 6.13, page 109 R (m)			equation 6.3 page 103 and section 6.5 estimated Q (m3/min)			estimated Q (gpm)		
t years	t days	t minutes	t seconds	median	min	max	median	min	max	median	min	max
	0	1.67E+00	1.00E+02	15.0	15.0	15.0	5.81E-03	1.16E-03	3.49E-02	92	18	553
	0.5	7.20E+02	4.32E+04	15.3	15.1	15.8	2.83E-04	5.65E-05	1.70E-03	4.5	0.9	26.9
	1	1.44E+03	8.64E+04	15.5	15.2	16.1	2.01E-04	4.02E-05	1.20E-03	3.2	0.64	19.1
	2	2.88E+03	1.73E+05	15.7	15.3	16.6	1.43E-04	2.86E-05	8.57E-04	2.3	0.45	13.6
	4	5.76E+03	3.46E+05	15.9	15.4	17.3	1.02E-04	2.04E-05	6.11E-04	1.6	0.32	9.7
	8	1.15E+04	6.91E+05	16.3	15.6	18.2	7.29E-05	1.46E-05	4.38E-04	1.2	0.23	6.9
	16	2.30E+04	1.38E+06	16.9	15.8	19.6	5.24E-05	1.05E-05	3.15E-04	0.8	0.17	5.0
0.1	32	4.61E+04	2.76E+06	17.6	16.2	21.4	3.79E-05	7.59E-06	2.28E-04	0.60	0.12	3.6
0.2	64	9.22E+04	5.53E+06	18.7	16.7	24.1	2.77E-05	5.53E-06	1.66E-04	0.44	0.09	2.6
0.4	128	1.84E+05	1.11E+07	20.3	17.4	27.9	2.04E-05	4.08E-06	1.22E-04	0.32	0.06	1.94
0.7	256	3.69E+05	2.21E+07	22.4	18.3	33.2	1.52E-05	3.04E-06	9.13E-05	0.24	0.05	1.45
1.4	512	7.37E+05	4.42E+07	25.5	19.7	40.8	1.15E-05	2.31E-06	6.92E-05	0.18	0.04	1.10
2.8	1024	1.47E+06	8.85E+07	29.9	21.7	51.4	8.89E-06	1.78E-06	5.34E-05	0.14	0.03	0.85
5.6	2048	2.95E+06	1.77E+08	36.0	24.4	66.5	6.99E-06	1.40E-06	4.19E-05	0.11	0.02	0.66
11.2	4096	5.90E+06	3.54E+08	44.7	28.3	87.9	5.61E-06	1.12E-06	3.36E-05	0.09	0.02	0.53
22.4	8192	1.18E+07	7.08E+08	57.1	33.8	118	4.58E-06	9.17E-07	2.75E-05	0.07	0.01	0.44

Flow from passive capture system as a function of time
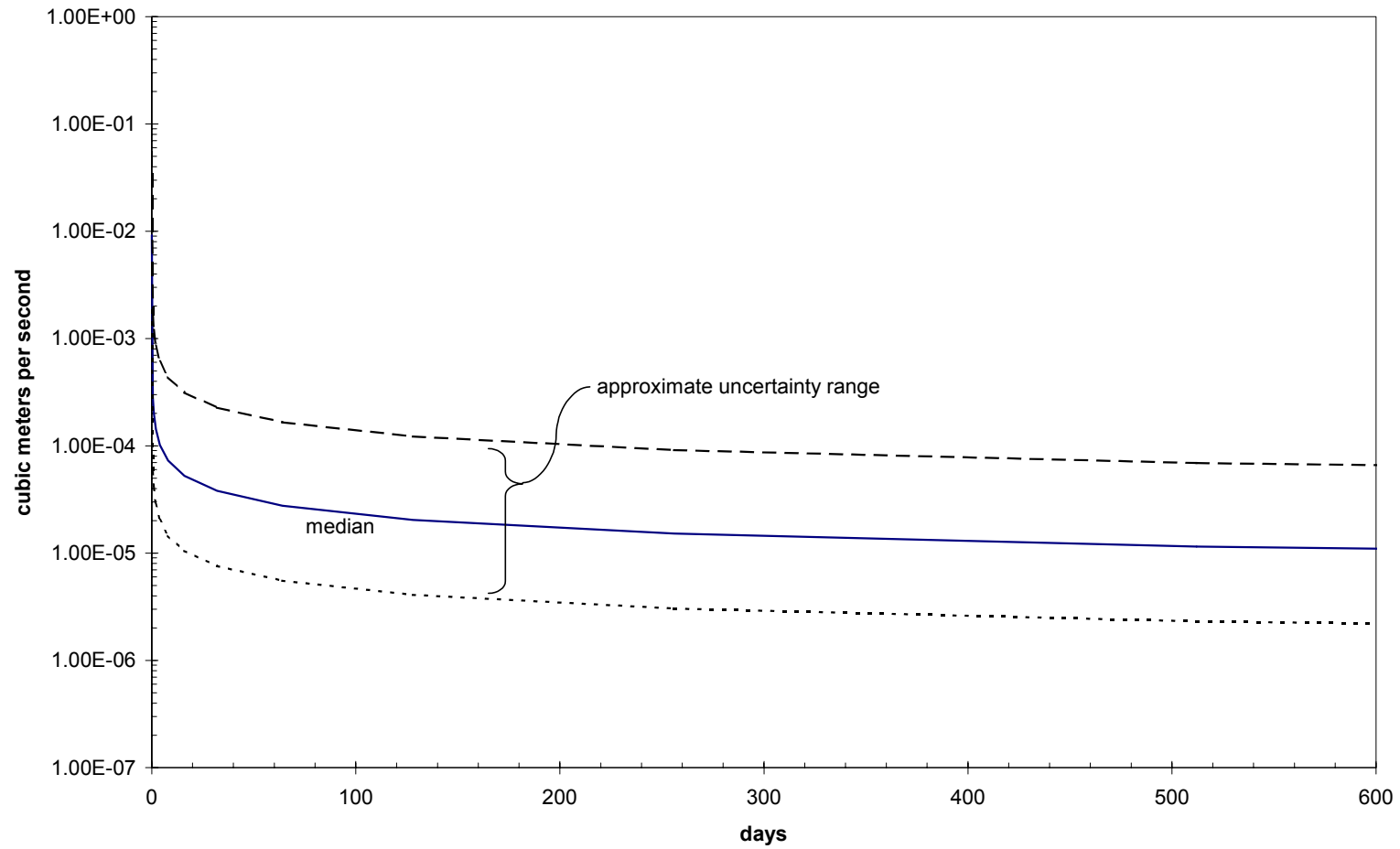
Flow from passive capture system as a function of time
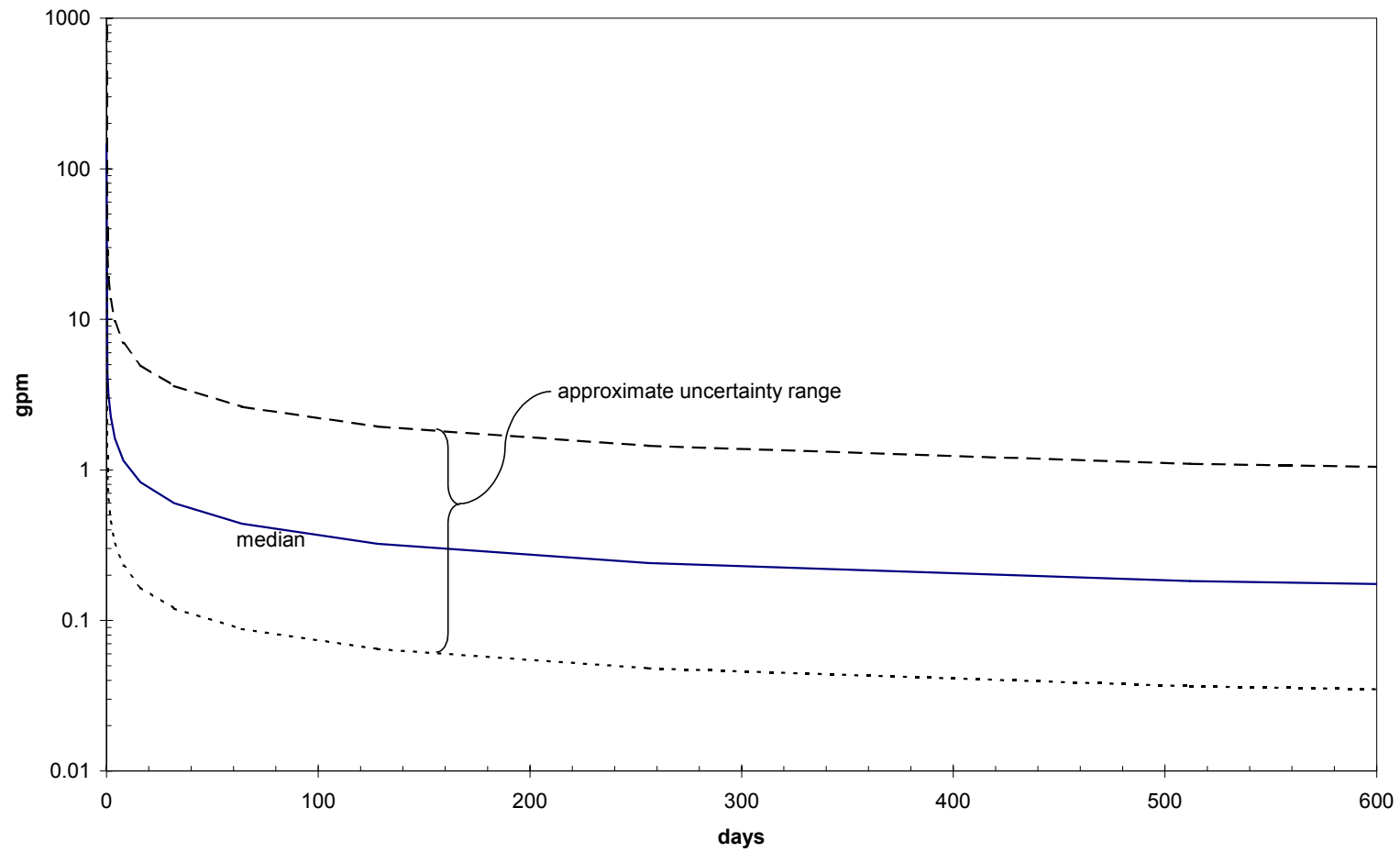
Approximate radius of influence
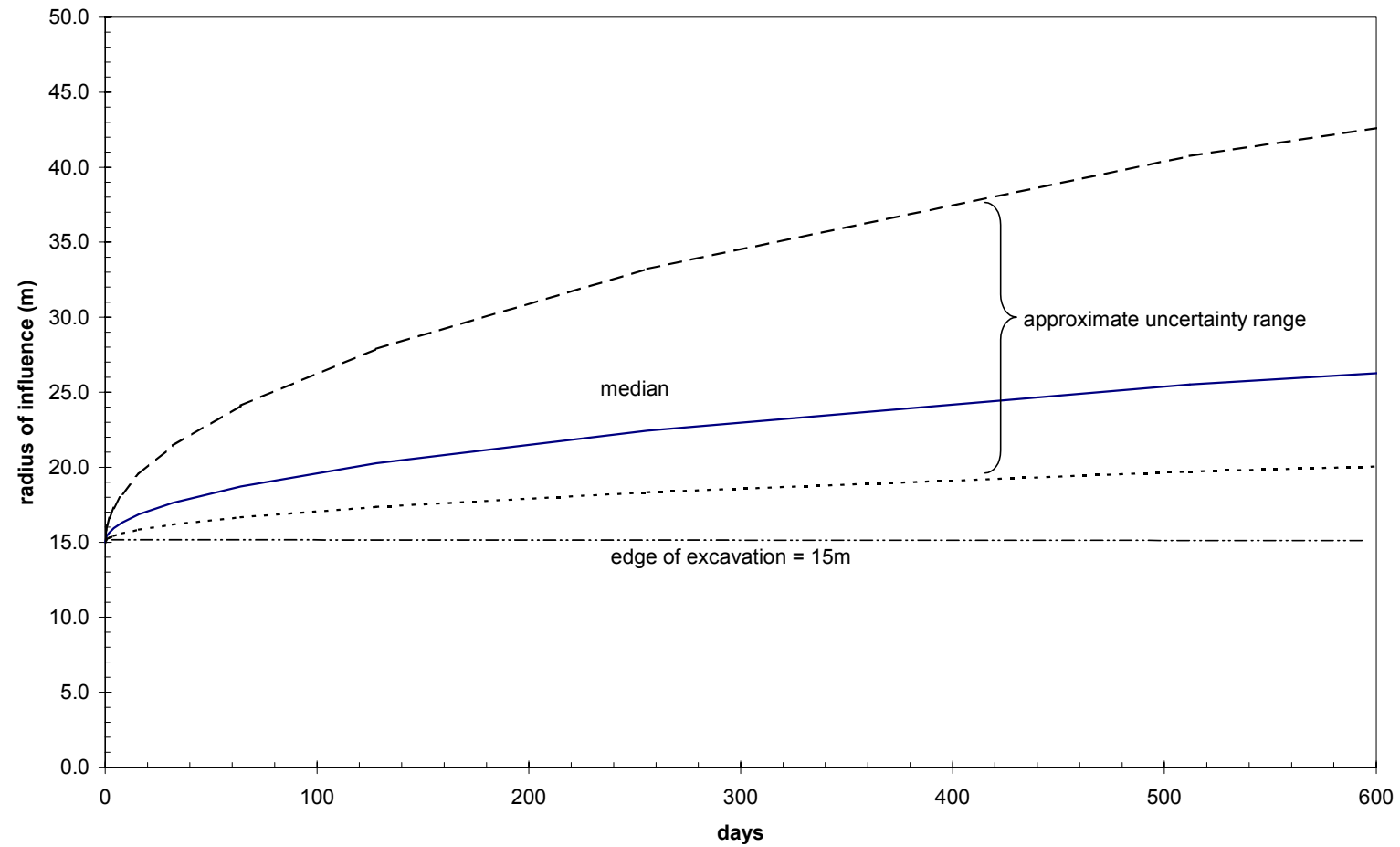
Approximate radius of influence
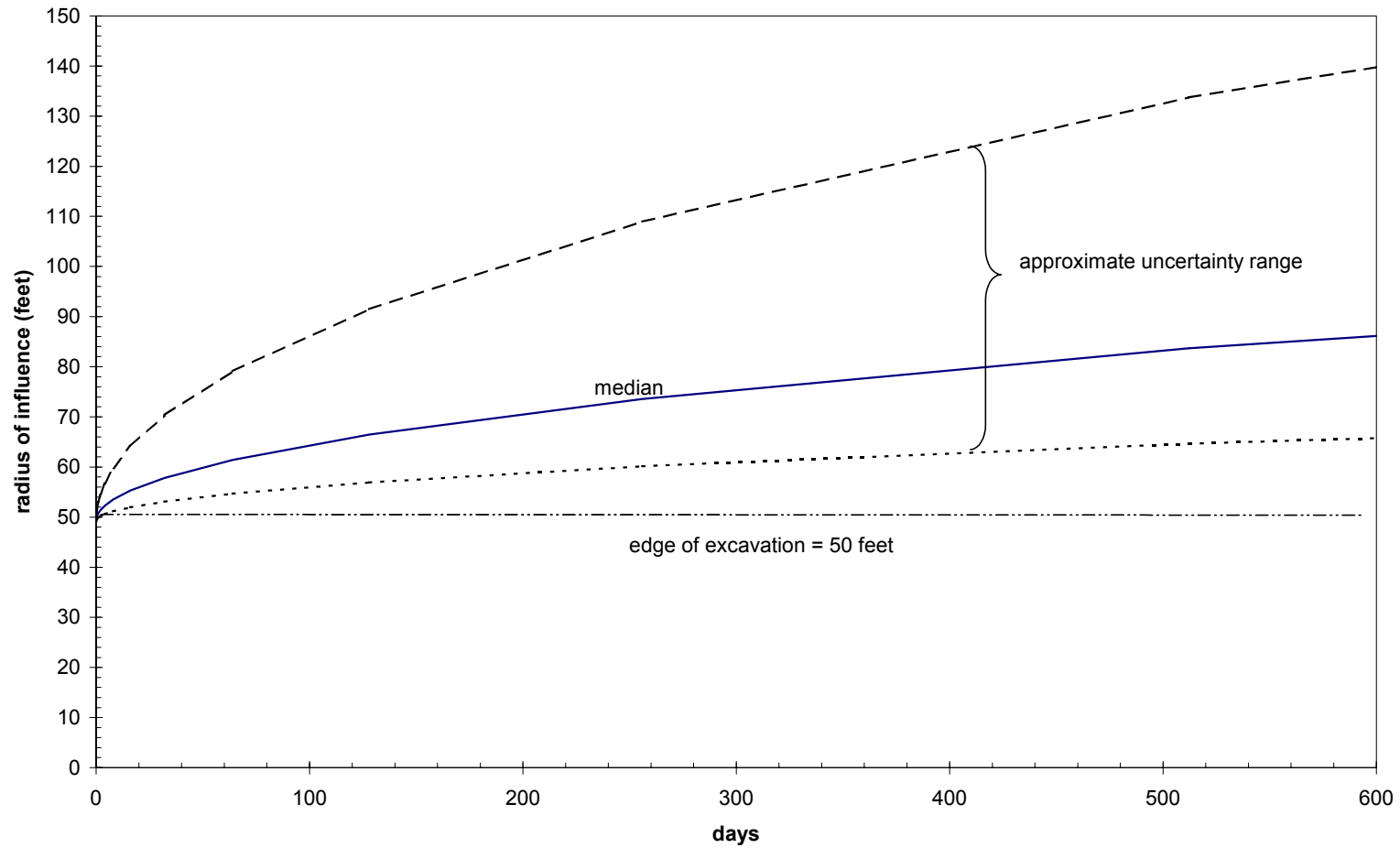
APPENDIX D –Technical Assistance Team Members

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Bill Frederick	USACE	Hydrogeology
Bob Steiner	WVNSCO	Environmental engineering
Joe Towarnicky	Sharp and Associates	Geotechnical engineering
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